



Augite-anorthite glass-ceramics from residues of basalt quarry and ceramic wastes

Gamal A. Khater^{1,*}, Mamduh O. Abu Safiah², Esmat M.A. Hamzawy¹

¹Glass Research Department, National Research Centre, Dokki, Cairo 12622, Egypt

²Saudi Geological Survey, Saudi Arabia

Received 27 April 2015; Received in revised form 14 June 2015; Accepted 27 June 2015

Abstract

Dark brown glasses were prepared from residues of basalt quarries and wastes of ceramic factories. Addition of CaF_2 , Cr_2O_3 and their mixture $\text{CaF}_2\text{-Cr}_2\text{O}_3$ were used as nucleation catalysts. Generally, structures with augite and anorthite as major phases and small amount of magnetite and olivine phases were developed through the crystallization process. In the samples heat treated at 900°C the dominant phase is augite, whereas the content of anorthite usually overcomes the augite at higher temperature (1100°C). Fine to medium homogeneous microstructures were detected in the prepared glass-ceramic samples. The coefficient of thermal expansion and microhardness measurements of the glass-ceramic samples were from 6.16×10^{-6} to $8.96 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$ (in the $20\text{--}500^\circ\text{C}$) and 5.58 to 7.16 GP, respectively.

Keywords: crystallization, anorthite, augite, glass-ceramics, basalt, ceramic waste

I. Introduction

Since the early 1960s, using waste to prepare glass-ceramics has developed in Russia, by employing slag of ferrous and non-ferrous metallurgy, ashes and wastes from mining and chemical industries [1]. Lately, the waste of coal combustion ash, fly ash and filter dusts from waste incinerators, mud from metal metallurgy, pass cement dust, different types of sludge and glass cullet or mixtures of them have been considered for the production of glass-ceramics [2–4]. Using waste to prepare glass-ceramics is significant for industrial applications as well as for environment protection and scientific importance with proper correction of the chemical composition [5,6].

Basalts are the main raw materials for the iron-rich glass and glass-ceramic materials. They are characterized by low viscosity, which allows production of polycrystalline materials by applying short production cycles at low temperature. For these reasons, many researchers continue to study the melting and the crystallization behaviour of different igneous rocks, and to characterize the obtained materials [7].

Because glass and glass-ceramics are known to have many commercial applications, the transformation of

waste into glass or glass-ceramics provides the opportunity of making useful, marketable products.

Ceramic waste materials used in this investigation are formed as waste materials from Saudi Ceramic plant Saudi Arabia formed during the manufacturing of sanitary ware ceramics. This waste accumulates in large quantities and possesses serious problems to the surrounding environment.

The use of waste materials such as ceramic waste, glass cullet, blast-furnace slag and by-pass cement dust for the production of glass-ceramic materials is of great economic technological and scientific importance through proper correction of chemical batch composition.

Research and development pertaining to glass-ceramic materials have been underway for more than three decades [8]. The fabrication technology of glass-ceramics, the glass composition, the nature of the nucleating agent and the thermal history, all greatly affect the microstructure and properties of these materials [9]. The internal crystallization can usually be achieved with a simple two-step heat treatment. In the first step, namely the nucleation step, the mobility of atoms in the glass is sufficient for embryo formation and subsequent nuclei stabilization. In the second step, the nuclei grow to crystals of desired sizes homogeneously dispersed in the glass volume [10]. It is obvious that internal crys-

* Corresponding author: tel: +2 01099291305, fax: +2 0233370931, e-mail: j.khater@yahoo.com

Table 1. Base glass composition

Raw materials [wt.%]		Calculated oxides constituents of base glass G0 [wt.%]							
Basalt waste	Ceramic waste	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O
80.00	20.00	50.75	17.28	9.62	1.31	9.01	6.71	3.08	1.07

tallization will be greatly facilitated by using suitable nucleating agents. Some investigations carried out in the field of nucleation in the ternary SiO₂-MgO-CaO and related systems have shown the relative difficulty of initiating internal nucleation and bulk crystallization in some glass-ceramic compositions of this system [11].

The composition of the above-mentioned glass-ceramics can mainly be located in the SiO₂-Al₂O₃-CaO-MgO system. Many investigators have studied the nucleation process in the SiO₂-Al₂O₃-CaO-MgO and related glass system. Cr₂O₃ is one of the most recommended oxides which according to the reports of many researchers is able to induce effective bulk nucleation in the glasses of SiO₂-Al₂O₃-CaO-MgO and related systems. Rezvani *et al.* [12] found that Cr₂O₃, Fe₂O₃ and TiO₂ are more effective in inducing bulk crystallization and Omar *et al.* [13] suggested that Cr₂O₃ favours pyroxene crystallization in quartz sand-dolomite-magnesite mixtures. Khater *et al.* [14,15] found that Cr₂O₃ and CaF₂ and their mixtures are more effective in SiO₂-Al₂O₃-CaO-MgO system based on industrial waste.

The use of raw materials, such as igneous or sedimentary rocks, for the production of glass-ceramics materials is of great economic, technological and scientific importance. With proper batch formulation, different types of igneous and sedimentary rocks can be successfully used for the production of crystalline-glass materials of different microstructures and mineralogical constitutions having a wide range of properties. Furthermore, the study of crystallization process taking place in rock melts and their corresponding glasses has a great contribution in petrology field. Minerals capable of wide isomorphs substitutions in their crystal structures, and having the desired properties, may be the bases for the production of many valuable crystalline-glass materials [16].

Due to the high chemical durability of natural basalts, basalt-like glass-ceramic materials were developed for nuclear waste disposal [17] and for vitrification of various hazardous industrial wastes [18].

In the previous paper [2], preparation of glass-ceramics materials from basaltic rocks and some industrial wastes was investigated. The aim of the present study is the preparation of glass-ceramics based on ceramic waste materials and basaltic rocks. The effect of

different additions of the nucleating agents Cr₂O₃, CaF₂ and their mixtures on the crystallization ability, phase assemblages and microstructure was investigated.

II. Experimental procedure

2.1. Glass preparation and batch calculation

Wastes basaltic rocks and ceramic waste from Saudi Ceramic Company, Saudi Arabia, were used as starting materials for the preparation of the investigated glass and glass-ceramics. Their chemical compositions are given in Table 1. The base glass (G0) was prepared by mixing of 80 wt.% of the basaltic rocks with 20 wt.% of the ceramic waste and their compositions are given in Table 2.

Nucleation agents such as CaF₂, Cr₂O₃ and their mixture, were used for the control of crystallization process and formation of augite-anorthite glass-ceramics. Different amounts of additives were incorporated in the base glass G0 and five different samples were obtained: G2F with 2 wt.% of CaF₂, G4F with 4 wt.% of CaF₂, G0.5C with 0.5 wt.% of Cr₂O₃, G1C with 1 wt.% of Cr₂O₃ and G2F0.5C with CaF₂-Cr₂O₃ mixture containing 2 wt.% CaF₂ and 0.5 wt.% of Cr₂O₃.

The weighed batch materials, after thorough mixing were melted in Pt crucibles in an electrically heated furnace at temperatures ranging from 1400 to 1450 °C for 1.5 to 2 h depending upon the nucleant involved. The melts containing Cr₂O₃ were rather more viscous than those containing CaF₂ and their mixtures therefore required higher temperatures and longer periods of melting. The homogeneity of the melt was achieved by swirling of the melt-containing crucible several times at about 20 min. intervals. After melting and refining, the bubble-free melt was cast onto a hot steel marver into buttons and rods. The hot glass samples were then transferred to a preheated electric muffle furnace for annealing.

2.2. Differential thermal analysis

Differential thermal analysis (DTA) was carried out by a Shimadzu DTG60 micro differential thermo-analyser. 60 mg of powdered glass sample, of grain size less than 0.60 mm and greater than 0.2 mm, were used against Al₂O₃ powder as a reference material. A heating rate of 10 °C/min was maintained for all runs. The heat-

Table 2. Chemical composition (wt.%) of the raw materials used for batch preparation

Raw material	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	CaO	MgO	Na ₂ O	K ₂ O	L.O.I. ^a
Residue of basaltic rocks	45.90	16.55	11.8	1.49	10.85	8.30	3.24	0.76	0.41
Ceramic waste	70.14	20.20	0.88	0.60	1.63	0.33	2.45	2.30	1.17

^aloss of ignition at 1000 °C

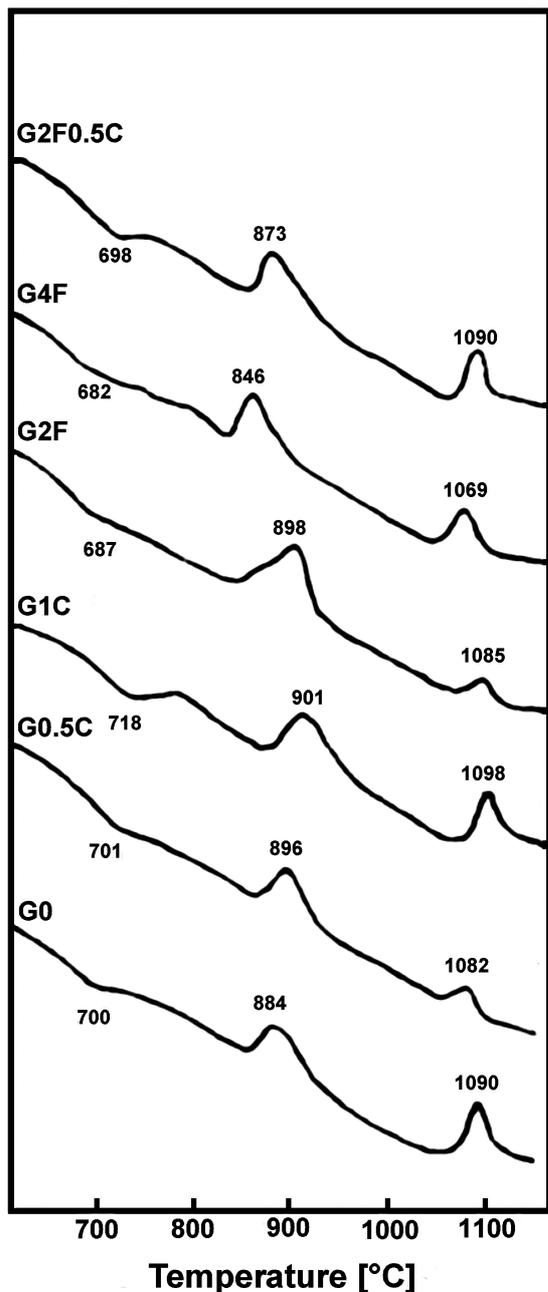


Figure 1. DTA curves of the investigated glasses

treatment of the glass samples were heated in a muffle furnace from room temperature to the required temperature and kept at the intended temperature for 2 h, after which the furnace was switched off and the samples were allowed to cool inside it to room temperature. The prepared glass samples were first soaked at 700 °C for 1 h and then at 900 and/or 1100 °C for 2 h.

2.3. X-ray diffraction analysis

Identification of crystalline phases precipitating in the course of crystallization was done by X-ray diffraction analysis of the powdered samples. X-ray diffraction patterns were obtained using a Bruker D8 Advance, Germany adopting Ni-filtered $\text{CuK}\alpha$ radiation. Instru-

ment settings of time constant 1 s, multiplier 1, range cps 400 and scanning speed 1°/min were used in this analysis.

It is worthy to mention that through X-ray analyses, all instrument settings were maintained for the analyses using a Si disk as an external standard (this was necessary to make the measurements based on the peak height more accurate). The reference data for the interpretation of X-ray diffraction patterns were obtained from ASTM X-ray diffraction Card file (1979). Other data obtained from several publications were also taken into consideration.

2.4. Scanning electron microscope

Scanning electron microscope (SEM model XL30, Phillips Holland) was used to evaluate the microstructure of crystalline samples at 1100 °C. The fresh fracture surface of the samples was etched chemically with acidic solution (1% HF + 1% HNO_3) for 1 s. The investigated samples were then dried and finally covered with a gold film for SEM examination.

2.5. Thermal expansion coefficient and hardness

Measurements of thermal expansion coefficient (CTE) of the glass-ceramics were carried out using a thermo-dilatometric analyser (Netzsch DIL 402 PC, Germany), using a fused silica bar as a standard.

Indentation microhardness of the investigated samples was measured by Vicker's microhardness indenter (Shimadzu, Type-M, Japan) using load 100 g and loading time of 15 s.

III. Results and discussion

Figure 1 shows the DTA curves for the various specimens were studied in this work. It can be noticed that the nucleation occurs in the temperature range from 682 to 718 °C, while crystallization occurs at temperatures between 846 and 1098 °C (Table 3).

The crystallization temperature of the base glass G0, according to DTA results, was at 884 °C and 1090 °C. XRD analysis of the sample G0 heat-treated at 900 °C confirmed presence of augite as a major phase and small amount of magnetite and olivine, whereas at 1100 °C major phases are augite and anorthite and a little amount of magnetite and olivine can be observed (Figs 2,3 and Table 4). Thus, it can be concluded that the first exothermic peak (Fig. 1) refers to the formation of augite as a major phase whereas, the second peak refers to the formation of anorthite as a major phase.

Calcium fluoride was incorporated in the base glass in amounts of 2 and 4 g /100 g of glass oxide (Table 3). Generally, it facilitates the melting process and decrease the temperature of beginning of crystallization of the glasses. It reduces the melting temperature and also the viscosity of the resultant melt in comparison with CaF_2 -free glasses. The endothermic peak temperatures (Table 3) shift from 700 in the base glass G0 to 687 and 682 °C in the GF2 and GF4 glasses, respec-

Table 3. Nucleating agent additions/100 g base glass and DTA results

Glass No.	Type of nucleator [g/100 g glass]	DTA endo-thermic peak [°C]	DTA-exothermic peak [°C]
G0	—	700	884, 1090
G2F	2 % CaF ₂	687	898, 1085
G4F	4% CaF ₂	682	846, 1069
G0.5C	0.5% Cr ₂ O ₃	701	896, 1082
G1C	1% Cr ₂ O ₃	718	901, 1098
G2F0.5C	0.5% Cr ₂ O ₃ + 2% CaF ₂	687	873, 1090

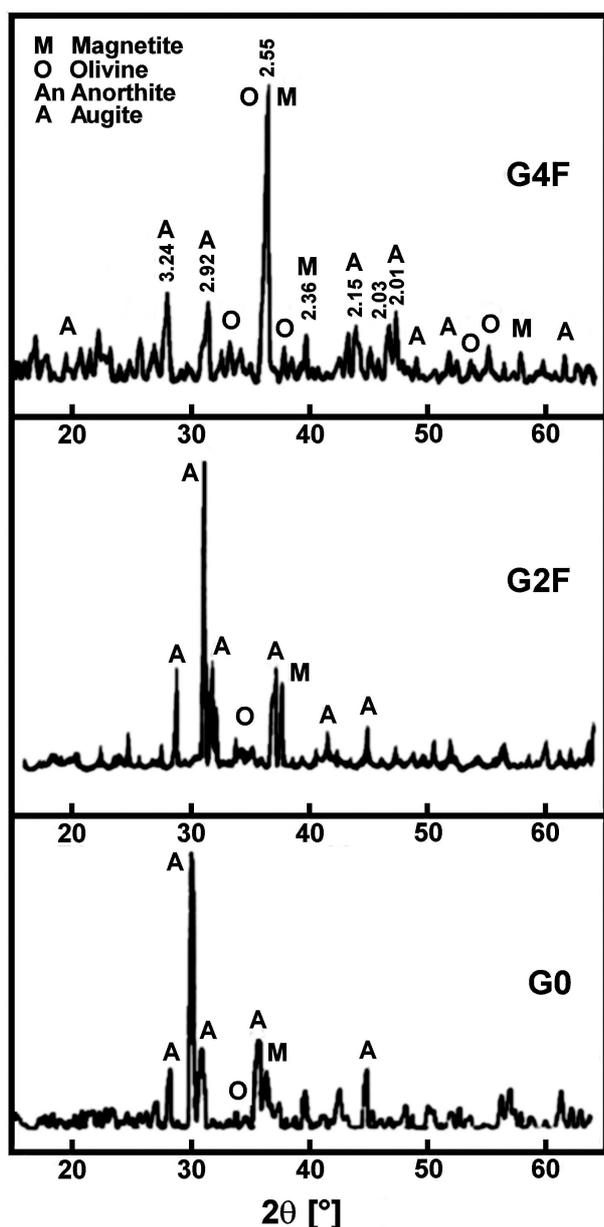


Figure 2. X-ray diffraction patterns of G0, G2F and G4F glasses heat-treated at 900 °C

tively. Also, the crystallization exothermic peaks of the base glass G0, observed at 884 and 1090 °C, shift to 898 / 1085 °C and 846 / 1069 °C in the glasses G2F and G4F, respectively (Fig. 1, Table 3). At lower temperature, 900 °C, the presence of 2% CaF₂ (the sample G2F) facilitated formation of augite as a major crys-

talline phase, besides olivine and magnetite as minor phases (Fig. 2). At higher temperature, 1100 °C, similar like in the base glass G0, augite and anorthite were developed. In the sample G4F containing higher percentages of CaF₂ (4 wt.%) formation of augite phase at 900 °C is retarded and higher amount of olivine and magnetite can be observed (Fig. 2). However, after heat-treatment at 1100 °C amount of anorthite is higher than augite and magnetite (Table 3). The SEM micrographs of the fluorine-containing samples, heat-treated at 1100 °C/2 h, show homogenous very fine grain microstructure in the sample G2F, whereas homogeneous pattern with well crystalline cubic crystal structure and skeletal fine grained mottled fabrics where developed in the sample G4F (Fig. 5).

Generally, the presence of fluorine helps in the formation of olivine and magnetite at low temperature and favoured formation of anorthite and magnetite at high temperature. This variability of mineral formation can be ascribed to the strong effect of fluorine ions on reducing the viscosity of the crystallizing glass. As a result it facilitates migration and diffusion of the ions and ionic complexes present to such an extent that crystallization of the structurally more complex silicates can take place, e.g. the anorthite and magnetite formation.

The addition of 0.5% Cr₂O₃ (the sample G0.5C) and 1% Cr₂O₃ (the sample G1C) to the base glass tends to shift T_g , glass transition temperature, to relatively higher values at 701 °C and 718 °C, respectively. In addition, the exothermic peaks shift to 896 / 1082 °C and 901 / 1098 °C for G0.5C and G1C, respectively (Fig. 1). The X-ray diffraction analysis of the crystallized Cr₂O₃-containing glasses, treated at 900 °C, indicates the formation of augite, olivine and magnetite (Table 3). At higher temperature, i.e. 1100 °C, intensities of anorthite lines (e.g. lines at 4.05, 3.77 and 3.21 Å) and olivine lines (e.g. lines at 2.77, 2.67 and 1.76 Å) are relatively strong, especially in the sample G1C with higher Cr₂O₃ content (Fig. 3). The SEM micrograph of the sample G0.5C shows homogenous fine grained microstructure after treatment at 1100 °C/2 h (Fig. 5c), while structure of the sample G1C contains well defined crystalline fabrics and ribbon within glassy matrix (Fig. 5).

The beneficial effect of Cr₂O₃ additions in inducing fine-grained bulk crystallization as well as its influence on the observed phase composition may be due to one or more of the following reasons. It is well known that in some super cooled silicate melts and glasses, Cr₂O₃

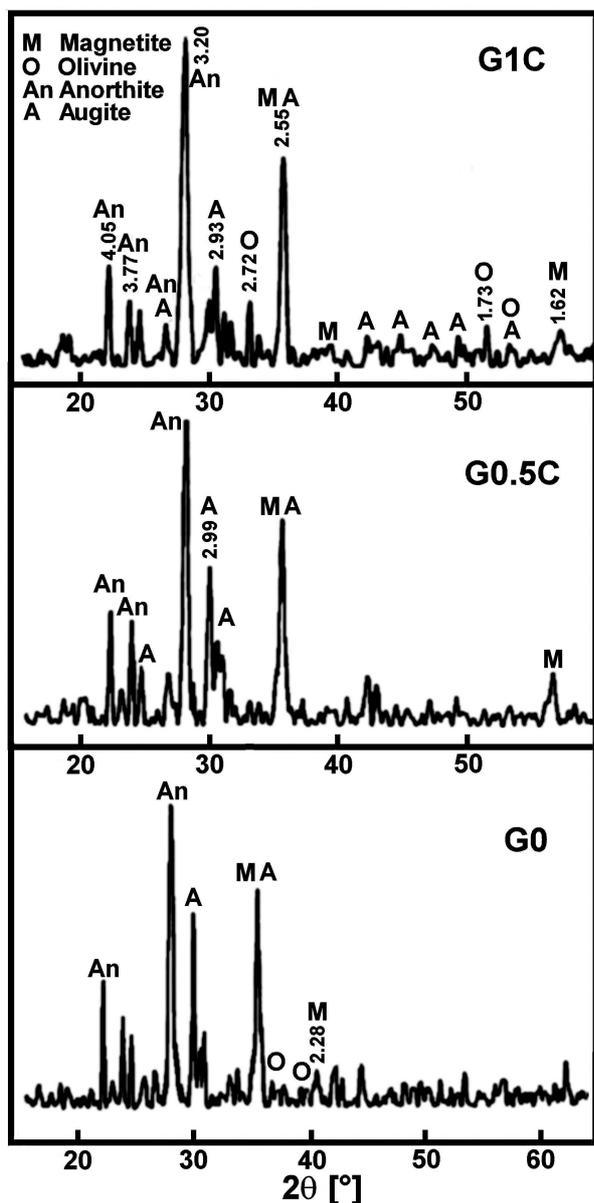


Figure 3. X ray diffraction patterns of G0, G0.5 and G1.0 glasses heat-treated at 1100 °C

may be completely miscible at high temperatures, but rapidly separates out at lower temperatures, either in the form of Cr-containing minute crystalline phases or as Cr-rich amorphous colloidal droplets [19] which act as sites for the subsequent crystallization of the major phases. The great affinity that chromium can be combined with other cations, such as Mg^{2+} , Fe^{2+} , Fe^{3+} and Al^{3+} , helps the formation of minute spinel-like phases of the general formation $(Mg,Fe)(Al,Fe,Cr)_2O_4$, which can readily crystallize out and act as crystallization centers or nuclei for the main crystallizing phases. According to McMillan [20] chromium can exist in glass as an interstitial cation of high field strength having trivalent and hexavalent states. The Cr^{3+}/Cr^{6+} ratio depends upon the melting conditions and a glass composition and may increase by increasing the melting temperatures and soaking times. Chromium in the hexavalent state (Cr^{6+}) has

Table 4. The crystalline phases developed in the glasses heat treated at 900 and 1100 °C

Glass No.	Heat-treatment		Identified phases ^a
	Parameters	[°C, h]	
G0	900 °C, 2 h		Au - Mag - Ol
	1100 °C, 2 h		An- Au- Ol- Mag
G0.5C	900 °C, 2 h		Au - Mag- Ol
	1100 °C, 2 h		An- Au- Ol- Mag
G1C	900 °C, 2 h		Au - Mag- Ol
	1100 °C, 2 h		An- Au- Ol- Mag
G2F	900 °C, 2 h		Au - Mag- Ol
	1100 °C, 2 h		Au- An- Mag- Ol
G2F0.5C	900 °C, 2 h		Au - Mag- Ol
	1100 °C, 2 h		An- Au- Ol- Mag
G4F	900 °C, 2 h		Mag- Au- Ol
	1100 °C, 2 h		An- Au- Ol- Mag

^aAu: augite, An: anorthite, Mag: magnetite, Ol: olivine

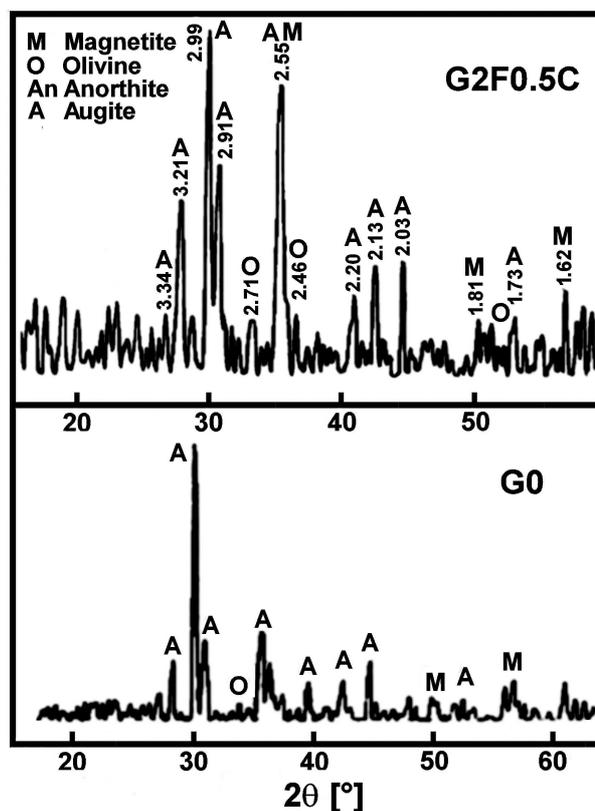


Figure 4. X ray diffraction patterns of G0 and G2F0.5 glasses heat-treated at 900 °C

higher field strength and hence it would occupy an interstitial position, exerting a marked ordering effect upon the oxygen ions surrounding it. Under these circumstances an amorphous chromium-rich phase separates out from the glass.

The addition of 0.5% Cr_2O_3 and 2% CaF_2 mixture to the base glass enhances the crystallization ability. From DTA results, it can be noticed that the exothermic crystallization peaks are displaced to lower temper-

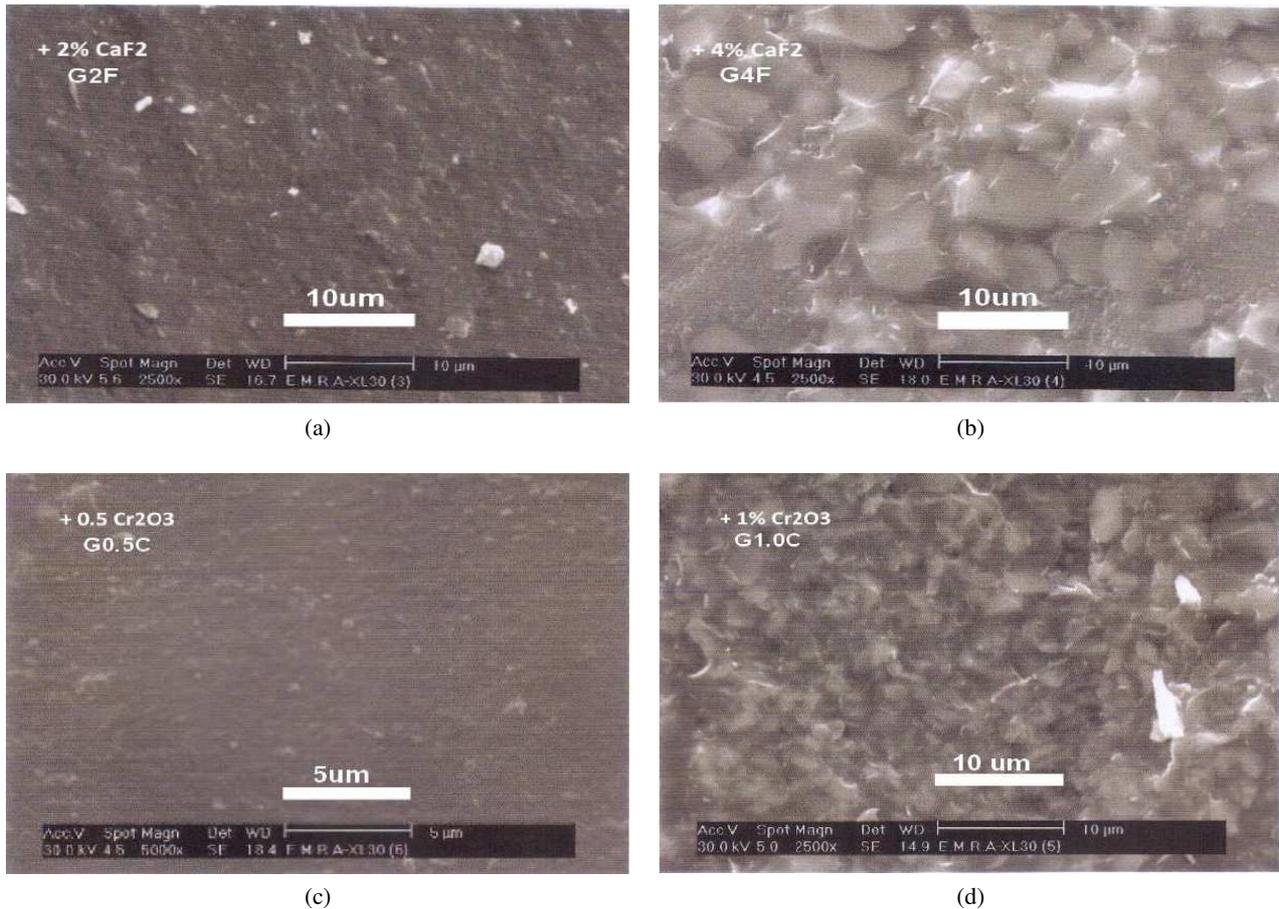


Figure 5. SEM micrographs of G2F (a), G4F (b), G0.5C (c) and G1.0C (d) heat-treated at 1100 °C/2 h

Table 5. CTE and microhardness values of the glasses treated at 900 °C

Glass No.	CTE [10 ⁻⁶ °C ⁻¹]	VH [GP]
G0	6.61	5.58
G4F	8.96	6.12
G1C	8.35	7.16
G2F0.5C	8.56	6.85

atures when compared with those of the base glass G0 or glass containing 0.5% Cr₂O₃ (the sample G0.5C) (Fig. 1). The glass containing this mixture facilitated augite solid solution as the major crystalline phase and minor amounts of magnetite and olivine at lower temperature 900 °C/2 h (Table 3). At higher processing temperature, 1100 °C/2 h, the mixture favoured the formation of anorthite and retarded augite formation (Fig. 4).

The thermal expansion coefficients (CTE) of the selected glass-ceramics are 6.61×10⁻⁶ °C⁻¹ and 8.96×10⁻⁶ °C⁻¹ in the glass-ceramics G0 and G4F, respectively (Table 5). In the previous work [21], the glass-ceramics prepared from basalt composed mainly of clinopyroxenes exhibited thermal expansion coefficients in the range 7.23–8.52×10⁻⁶ °C⁻¹ (in temperature range 0–300 °C). In addition, the CTE of diopside and anorthite are reported by Rigby and Green [22] to be

8.3.0×10⁻⁶ °C⁻¹ and 6.4×10⁻⁶ °C⁻¹, respectively. Thus, the thermal expansion behaviour of the investigated glass-ceramics more or less follows the previously published results.

The microhardness values were found to be in the range from 5.58 to 7.16 GP. These high values indicate that the investigated glass-ceramics have high abrasion resistance and the possible applications under hard mechanical conditions.

IV. Conclusions

In the present work, the presence of CaF₂ helps in the formation of anorthite and magnetite, and retarded augite formation, and leads to the formation of fine to medium homogenous microstructures. On the other hand, the presence of low concentration of Cr₂O₃ (0.5 wt.%) is highly effective as catalyst for initiating crystallization centers that induce volume crystallization and formation fine grained glass-ceramics. When Cr₂O₃ is present in higher concentrations (1.0 wt.%), it favours anorthite formation and retarded augite crystallization. Mixtures of the nucleant species 0.5% Cr₂O₃ and 2% CaF₂ can lead to the formation anorthite due to CaF₂, which also facilitates the crystallization process and favours reaching thermodynamic equilibrium.

The investigated glass-ceramics have thermal

expansion coefficients ranging from 6.16×10^{-6} to $8.96 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ (in the 20–500 $^\circ\text{C}$) and good microhardness values ranging from 5.58 to 7.16 GP.

References

1. E. Bernardo, R. Castellan, S. Herglich, "Sintered glass-ceramics from mixtures of waste", *Ceram. Int.*, **33** (2007) 963–968.
2. G.A. Khater, A. Abdel-Motelib, A.W El Manawi, M.O.A. Abu Safiah, "Preparation of glass-ceramics materials from basaltic rocks and some industrial waste", *Ceram. Int.*, **38** (2012) 1128–1134.
3. J.K. Yang, D.D. Zhang, J. Hou, B.P. He, B. Xiao, "Preparation of glass-ceramics from red mud in the aluminum industries", *Ceram. Int.*, **34** (2008) 125–130.
4. G.A. Khater, "Glass-ceramics in the CaO-MgO-Al₂O₃-SiO₂ system based on industrial waste materials", *J. Non-Cryst. Solids*, **356** (2010) 3066–3070.
5. H. Liu, H. Lu, D. Chen, H. Wang, H. Xu, R. Zhang, "Preparation and properties of glass-ceramics derived from blast furnace slag by a ceramic-sintering process", *Ceram. Int.*, **35** (2009) 3181–3184.
6. G.A. Khater, "Diopside-anorthite-wollastonite glass-ceramics based on waste from granite quarries", *Glass Technol. - Europe. J. Glass Sci. Technol. A.*, **51** [1] (2010) 6–11.
7. S.A.M. Abdel-Hameed, I.M. Bakr, "Effect of alumina on ceramic properties of cordierite glass-ceramic from basalt rock", *J. Eur. Ceram. Soc.*, **27** (2007) 1893–1897.
8. M.L. Ovecoglu, B. Kuban, H. Ozer, "Characterization and crystallization kinetics of a diopside-based glass-ceramic developed from glass industry raw materials", *J. Eur. Ceram. Soc.*, **17** (1997) 957–962.
9. J.I. Chu, H.C. Park, C.C. Sorrell, "DTA study of nucleation and crystallization of MgO-CaO-SiO₂-P₂O₅ glass-ceramics containing ZrO₂, BaCO₃ and Li₂CO₃", *Int. Ceram. Monogr.*, **1** (1994) 585–590.
10. C. Leonelli, T. Manfredini, M. Paganelli, "Crystallization of some anorthite-diopside glass precursors", *J. Mater. Sci.*, **26** (1991) 541–546.
11. G. Baldia, E. Generali, "Effects of nucleating agents on diopside crystallization in new glass-ceramics for tile-glaze application", *J. Mater. Sci.*, **30** (1995) 3251–3255.
12. M. Rezvani, B. Eftekhari-Yekta, M. Solati-Hashjin, V.K. Marghussian, "Effect of Cr₂O₃, Fe₂O₃ and TiO₂ nucleants on the crystallization behavior of SiO₂-Al₂O₃-CaO-MgO(R₂O) glass-ceramics", *Ceram. Int.*, **31** (2005) 75–80.
13. A. Omar, A.W. Elshennawi, G.A. Khater, "The role of Cr₂O₃, LiF and their mixtures on crystalline phase formation and microstructure in Ba, Ca, Mg aluminosilicate glass", *Br. Ceram. Trans. J.*, **90** (1991) 179–183.
14. G.A. Khater, "Influence of Cr₂O₃, LiF, CaF₂ and TiO₂ nucleants on the crystallization behavior and microstructure of glass-ceramics based on blast-furnace slag", *Ceram. Int.*, **37** [7] (2011) 2193–2199.
15. G.A. Khater, E.M.A. Hamzawy, "Effect of different nucleation catalysts on the crystallization behavior, within the CaO-MgO-Al₂O₃-SiO₂ system", *Silicate Ind.*, **73** [7-8] (2008) 103–107.
16. G.A. Khater, "The use of some Saudi basalts for the production of glass ceramic materials", *Egyptian Mineral.: J. Mineral. Soc. Egypt*, **12** (2000) 267–279.
17. M.I. Ojovan, W.E. Lee, *New Development in Glassy Nuclear Waste Forms*, Nova Scientific Publisher, New York, 2007.
18. P. Kavouras, P. Komninou, K. Chrissafis, "Microstructural changes of processed vitrified solid waste products", *J. Eur. Ceram. Soc.*, **23** (2003) 1305–1311.
19. L.A. Zhunina, V.N. Shara, V.F. Tsikov, N.N. Khripkova, "Crystallization of glasses of composition CaO-MgO-Al₂O₃-SiO₂ in the presence of Cr₂O₃ with formation of a stable pyroxene phase", pp. 192 in *The Structure of Glass Consultants Bureau*, N.Y.3, 1964.
20. P.W. McMillan, *Glass-Ceramics*, 2nd Ed., Academic Press, London, England, 1979.
21. G.H. Beall, H.L. Rittler, "Process for forming a basaltic glass-ceramic product", U.S. Patent 3.557,579, Jan. 1971.
22. G.R. Rigby, A.T. Green, "The thermal expansion characteristics of some calcareous and magnesian minerals", *Trans. Brit. Ceram. Soc.*, **41** (1942) 123–143.

