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Thermal and chemical properties of diopside-wollastonite glass-ceramics in the SiO_2–CaO–MgO system from raw materials

S.A.M. Abdel-Hameed*, A.A. El-kheshen

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

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Abstract

The crystallization process of ternary system SiO_2–CaO–MgO from waste raw materials was investigated by DTA and polarizing microscope and characterized by chemical durability for glasses and glass-ceramics. The effects of compositional changes on bulk crystallization and growth morphology were also studied. β-wollastonite and diopside, were identified after heat-treatment. The coarse grained morphology with directional surface crystallization was observed. Studying of chemical durability shows that, the weight loss increased by increasing CaO content on the expense of MgO in both acidic or alkaline solution.

Keywords: C. Thermal properties; C. Chemical properties; D. Glass ceramics; SiO_2–CaO–MgO system

1. Introduction

The present paper describes an attempt to show the possibility of using raw materials such as dolomite and limestone for the production of wall-covering glass-ceramic materials which, in addition to their attractive appearance similar to that of granite, possess physico-mechanical and chemical properties exceeding those of natural wall-covering materials.

Japanese make glass-ceramic from β-wollastonite as the main phase [1,2] and a similar material developed by a Bulgarian team [3], the major crystalline phase in this case being diopside ($CaO{\cdot}MgO{\cdot}2SiO_2$). These two kinds of materials have an appearance similar to that of natural marble and physico-mechanical and thermal properties that considerably surpass the properties of natural wall-covering materials and are close to those of slagsitalls.

The purpose of the present study is to demonstrate the possibility of obtaining wall-covering glass-ceramics from dolomite and limestone and study DTA, microstructure and chemical durability of glass and glass-ceramics.

2. Experimental

The raw materials used to prepare the glass compositions were reagent grade. All batches (Table 1) were thoroughly mixed and melted in a platinum crucible in an electric furnace at 1500 °C for 3 h with occasional swirling 30 min. apart to ensure complete homogenization. The homogeneous glasses were normally cast into 2 cm discs and 10×1×1 cm rods and then annealed at 650 °C. It is worth mentioning that lower viscosities and good working traits were noticed especially when MgO is replaced by CaO i.e. when β-wollastonite is increased over diopside; wherein a longer glass fiber could be drawn over a relatively longer duration according to the adopted qualitative viscosity test [4].

The DTA runs were carried out under N_2 atmosphere, Netzech thermal analysis system. A heating rate of 10 °C/min, corundum as a reference material, a constant flow rate of pure N_2 (50 cc/min) and ≈70 mg of powdered samples were maintained.

The details of the microcrystalline structure and mineralogical constituents, whenever possible, were examined in thin sections by using a polarizing Carl-Zeiss research microscope. Chemical durability was studied for both glass and glass-ceramic samples immersed in 5% HCl and 5% NaOH solutions for 1 h at 95 °C.

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* Corresponding author. Fax: +202-3370931.
E-mail address: salwa_NRC@hotmail.com (S.A.M. Abdel-Hameed).

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Table 1
The chemical composition of glass samples in mol.%

Glass No.	Glass composition (mol.%)			
	CaO	MgO	SiO_2	Na_2O
G1	26.20	21.70	47.89	4.21
G2	28.47	19.42	47.87	4.24
G3	30.77	17.10	47.86	4.27
G4	33.10	14.76	47.85	4.29
G5	35.46	12.38	47.84	4.32

3. Results and discussion

The DTA traces of some of the investigated glasses are shown in Fig. 1. Almost all the DTA traces are somewhat similar in their general characteristics, exhibiting an endothermic peak in the range 697–785 °C and an exothermic peak in the range 902–907 °C. The endothermic reaction is believed to be caused by an increase in the capacity due to a transformation of the glass structure [5]. The exothermic reaction due to the crystallization effect is accompanied by the release of heat due to the lower free energy; the maximum crystallization rate is attained near the summit of the exothermal peak [6].

The DTA traces are compared here with the aim of elucidating the effects of the incorporation of CaO at the expense of MgO on the crystallization behavior. A broad exothermic effect indicates a sluggish crystallization propensity, a lower crystallization rate and/or a surface crystallization character, while a sharp exothermic peak signifies a higher crystallizability, a higher crystallization velocity and/or a bulk (volume) crystallization process [7]. On this basis, all the DTA traces (Fig. 1) immediately indicate that almost all the glasses are characterized by a high crystallization propensity, but with different degrees of crystallizabilities, depending on the CaO:MgO ratio. The effect of CaO:MgO ratio can easily be observed in the DTA traces of

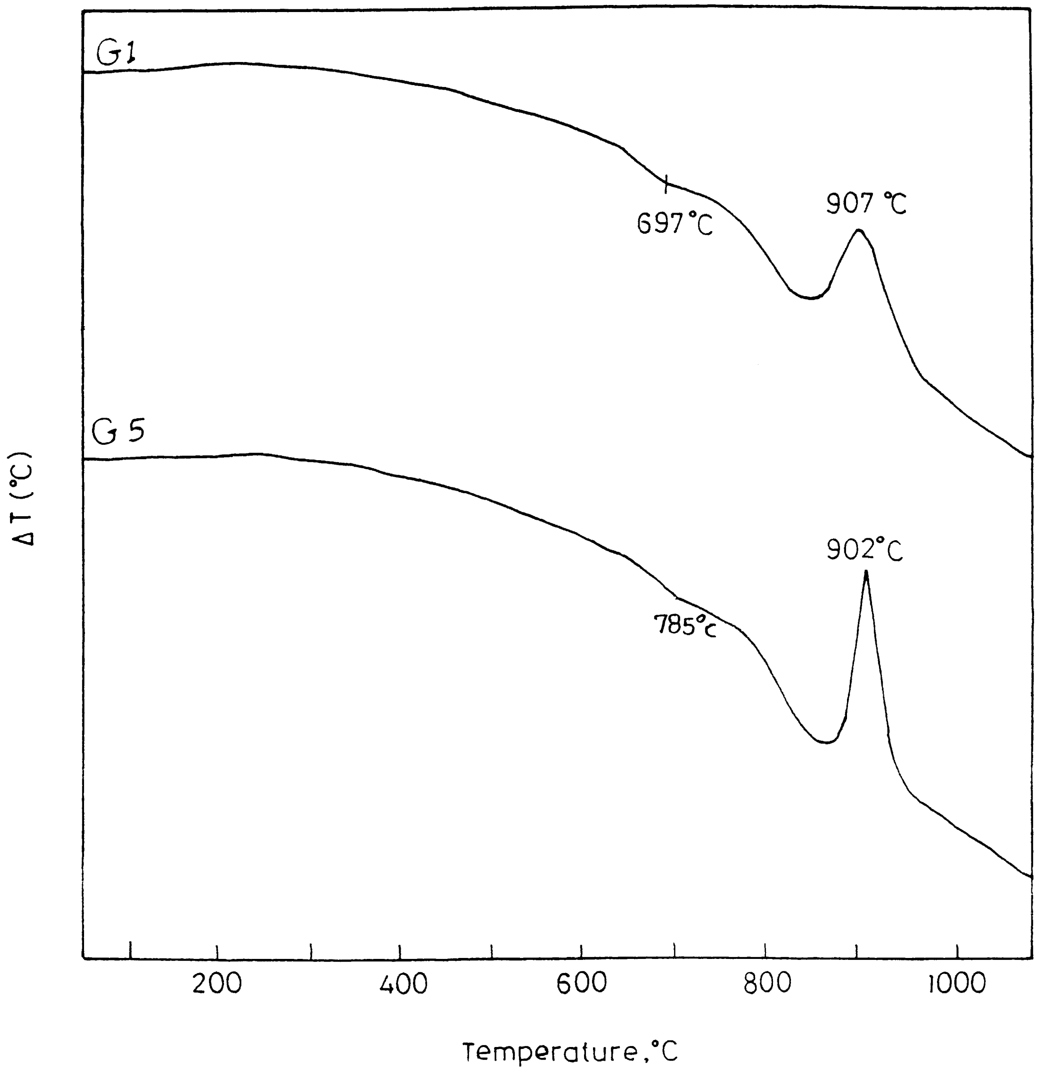

Fig. 1. DTA traces of G1 and G5.

glasses. The exothermic peaks intensified substantially and became more intense, sharper and lower in temperature with increase CaO:MgO ratio, that may be related to increase in the percent of β-wollastonite which may be work as nucleating agent to diopside crystallization. The increase of T_g temperature by decreasing CaO:MgO ratio, i.e. by increasing MgO at the expense of CaO, may be explained by the lowering effect of MgO on the viscosity of these glasses. As a result of the decrease in the viscosity, the mobilities and diffusion rates of the different ions and ionic complex-forming glasses will be markedly increased during the crystallization process, leading to higher crystallizabilities.

It was noticed, by the microscopic investigation of the crystalline glasses obtained from isothermal heat treatments at 1000 °C/2 h, that the increase of CaO:MgO ratio from G1→G5 (i.e. by increasing wollastonite over diopside phase) has an effect to produce much more fine-grained textures. For example, the microscopic examination of G2 heat-treated at 1000 °C/2h (Fig. 2a) shows coarse grained microstructure of fair-sized stellate pyroxenic growths while G4 shows interlocking fine-grained anhedral intergrowths of diopside stippled by lights of wollastonite. G5 with 50% wollastonite exhibit uniform fine-grained, of minute shapeless growths.

Studying the chemical durability of glasses revealed that, plotting the relation between the weight loss and the composition of the studied glass samples (Fig. 3a), by using 5% HCl as immersed solution, the weight loss increased by increasing the CaO content on the expense of MgO content and by using 5% NaOH as immersed solution, the weight loss increased also but in high percent more than that of HCl, these can be explained as follows.

The amount of silica extracted increases as the pH of the attacking solutions increase [8]. The effect of the different pH values of the solutions on the decomposition of glass samples, and the rate at which the constituents of the glass go into the solution, has been studied by number of investigators [9] and their results showed that all silicate glasses become partially susceptible to decomposition above pH ~ 9–10. The temperature used in this experiment was 98 °C, at this temperature the glass containing a high percent of CaO is less durable, and the durability increased with decreasing ionic size of the divalent used (Mg^{2+}). This behavior is in accordance with the thermodynamic

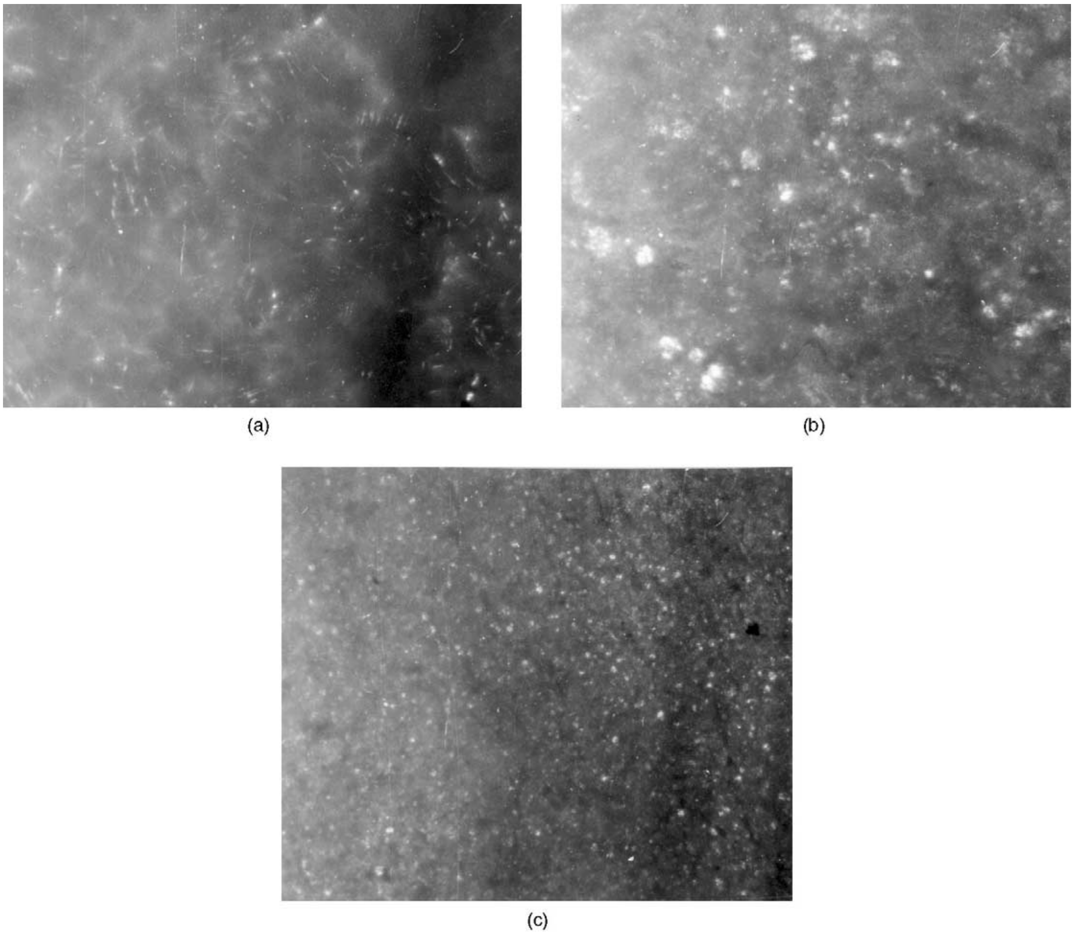

Fig. 2. Photomicrograph of (a) G2, (b) G4, (c) G5 heat treated at 1000 °C for 2 h (× 350).

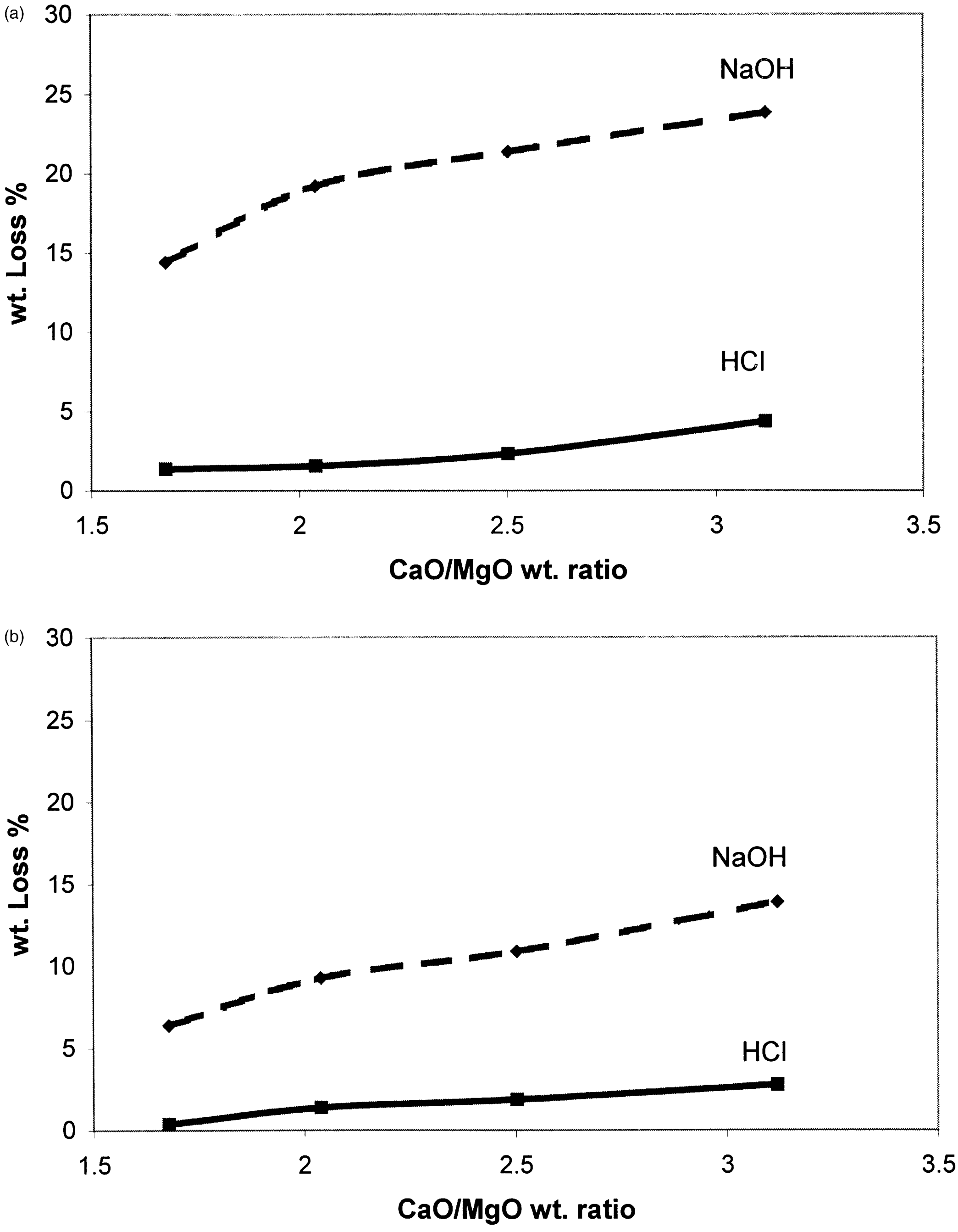

Fig. 3. (a) wt. Loss% of the glass as a function of CaO/MgO content in different media. (b) wt. Loss% of the glass-ceramic as a function of CaO/MgO content in different media.

stability of different binary alkaline earth silicates, as these divalent cations have weaker potential field than Si^{4+} but sufficiently strong to cause screening by OH^- ions rather than neutral water [10]. However, if the experiment was carried out at 60 °C, the same glasses indicate the apparent stability of CaO-containing glass compared with the MgO-containing glass. This is probably due to the fact that at lower temperatures the diffusion of the large Ca^{2+} ions becomes energetically restricted while the smaller Mg^{2+} ion can move through the leached layer relatively easily and can be extracted.

Fig. 3b shows the effect of the formation of crystalline phases on the chemical durability, through the relation between the composition and the weight loss of the glass ceramic, generally, it reveals that the weight loss percent is lower than that for the parent glass samples in both HCl and NaOH solutions. This seems to be due to the more bonding in glass ceramic network rather than the parent glass, due to the formation of crystalline phases during heat-treatment process.

In many cases, it is likely that when a glass-ceramic is chemically attacked, the initial effect is upon the glass phase present. This occurs because the early stages of attack involve ion exchange between hydrogen (or hydronium ions) and mobile cations (usually alkali metal ions) in the glass. The greater mobility of alkali metal ions (Na_2O) in the glass phase as compared with that of similar ions incorporated in crystal phases will lead to greater reactivity of the glass phase and hence to inferior resistance to chemical attack. The achievement of high chemical durability in glass ceramics indicates that, the chemical composition of the crystalline phases obtained favor good stability. McMillan [11] had indicated that, the glass ceramic, in general, possess good chemical stability and that they compare favorably in this respect with other ceramic type materials.

In our glass ceramic samples, two phases (wollastonite and diopside) appeared. As the diopside phase percent decreases at the expense of the wollastonite phase percent, the durability decreases but it shows more decrease in case of using 5% NaOH as immersed solution. These results indicate that an increase in the ratio of diopside to wollastonite is advantageous from the viewpoint of chemical corrosion resistance characteristic.

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