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Sintering behavior of SiO_2-CaO-MgO (Na_2O) glass–ceramics system

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Abstract

The influence of some nucleating agents on the sintering, crystallization and mechanical properties of SiO_2-CaO-MgO (Na_2O) glasses was investigated. It was found that the glass–ceramic containing Fe_2O_3 and Cr_2O_3 had desirable sintering behavior and reached to an acceptable density. However, the sinterability of specimens was degraded by addition of $CaF_2 + MoO_3$ and/or $V_2O_5 + MoO_3$ through reduction of crystallization temperatures of glasses. In these cases increasing of firing temperature led to reduction of the transition metal oxides and bloating of specimens.

Keywords: A. Sintering; C. Mechanical properties; D. Glass-ceramics; Crystallization

1. Introduction

Glass–ceramics of the SiO_2-CaO-MgO system are important materials, due to their special durability and mechanical properties arise from precipitation of diopside and wollastonite phases [1]. However, in spite of extensive work done on this system, yet bulk crystallization of these glasses is associated with some problems [2–5]. The present work has tried to overcome this problem by optimizing the sintering route. The method has some disadvantages: the surface area of glasses increase and size of crystalline particles is limited to the initial glass particle size distribution. As major advantage the need of bulk crystallization is eliminated [6]. Therefore, we have tried to overcome the crystallization problems of this glass system by use of various common nucleating agents and adjustment of sintering method.

2. Experimental procedure

2.1. Melting

The compositions of glasses studied are listed in Table 1. All of the raw materials used for preparation of the glasses were reagent grade. The weighed batch materials, after mixing, were melted in a platinum crucible in an electric furnace at 1400 °C for 1 h. The melts were then quenched in water to obtain frits.

2.2. Forming and analysis methods

The particle size measurements of the powdered glasses were carried out by a laser particle size analyzer (Fritsch, Analysette 22). The crystallization temperatures of the crystalline phase were determined by simultaneous thermal analysis, STA (Polymer Laboratories, model 1640) at a rate of 10 °K min^{-1}. The powder of glasses were pressed using laboratory uniaxial hydraulic press into 12 mm × 2 mm at final pressure of 65 MPa. Methyl cellulose (0.45 wt.%) was used as a binder.

Sintering was carried out in an electric furnace at a heating rate of 10 °K min^{-1} at 950, 1000, 1020, 1050, 1100 and 1120 °C. The soaking time was 3 h.

The crystallized samples resulting from the heat treatment were then studied by XRD using a powder diffractometer (Siemens D-500, Cu Kα radiation at 40 kV). Silicon powder was used as standard. The microstructure of the crystallized samples was studied by scanning electron microscopy (Cambridge, Stereoscan 360). The bulk and powder densities of sintered samples were determined by Archimedes method and gas pycnometer (Micromeritics, Accupyc 1330). The

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Table 1
Compositions (wt.%) of various glasses

Samples	SiO_2	CaO	MgO	Na_2O	MoO_3	Fe_2O_3	Cr_2O_3	WO_3	V_2O_5	CaF_2
A	59.68	12.23	15.02	5.08	–	4.00	4.00	–	–	–
B	59.68	12.23	15.02	5.08	–	6.00	–	2.00	–	–
C	59.68	12.23	15.02	5.08	4.00	–	–	–	4.00	–
D	59.68	12.23	15.02	5.08	4.00	–	–	–	–	4.00

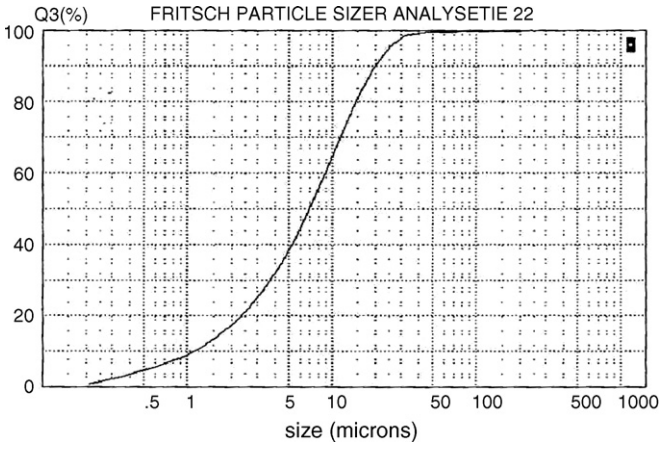

Fig. 1. Particle size distribution of glass powder.

rectangular specimens of dimensions 25 mm × 2.5 mm × 2.5 mm were used for flexural strength examinations in three-point bending in air using an Instron Universal Testing machine 1196. For each sample, six measurements were made.

A Vickers micro hardness tester with a diamond pyramid indenter (Buehler, Micromet 1) was used to measure micro hardness. The load was 100 g and the loading time was 30 s.

3. Results and discussion

With respect to the effect of glass particle size on its sinterability [7], the frits were grinded to a mean particle size of 7 μm (Fig. 1).

The crystallization temperature difference (ΔT) of the two different glass particle sizes characterized by DTA is known as a criterion for studying the mechanism of crystallization of a glass. It was argued that a ΔT less than 10 °K means that crystallization starts in the bulk. The crystallization peak temperature of glass particles smaller than 63 μm, and between 180 and 212 μm is shown in Table 2. According to the ΔT criterion, it seems that surface crystallization is the dominant mechanism in all glasses, and V_2O_5 and CaF_2 solely affects the

Table 2
Crystallization peak temperatures for two particle sizes of various samples

Samples	Particle size (μm)		T_p (°C)		ΔT
A	<63	180–212	894	918	24
B	<63	180–212	867	919	52
C	<63	180–212	838	864	26
D	<63	180–212	864	895	31

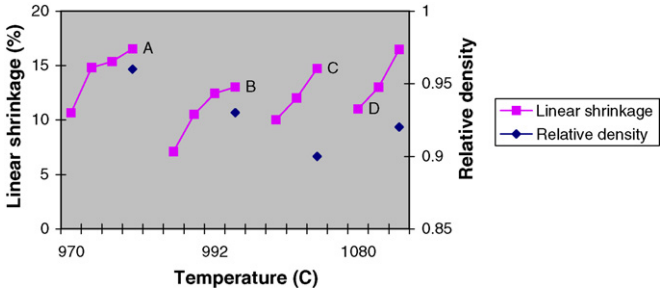

Fig. 2. Variation of linear shrinkage and relative density of glasses with firing temperature.

crystallization behavior through changing the surface tension and the viscosity of glasses [3]. Diopside and wollastonite are the main crystalline phases which precipitated after heat treatment of the glasses at their crystallization peak temperatures [2–5].

Fig. 2 depicts the sintering behavior of various glasses. Shrinkage is affected by the kind of nucleating agents used. By comparing the crystallization peak temperature of fine glass powders (Table 2) and their sintering behavior (Fig. 2) it can be concluded that sinterability depends on temperature at which crystallization started. It means that with increasing the crystallization temperature, the glassy phase would have enough time for viscous flow which leads to its complete densification [7,8]. The comparison of relative density of glasses shows that glass A reaches an acceptable densification at about 100 °K above its crystallization peak temperature, the relative density of the other glasses is far below 100% even about 200 °K above their crystallization peak temperatures. A blistered surface was observed in the specimens B, C and D

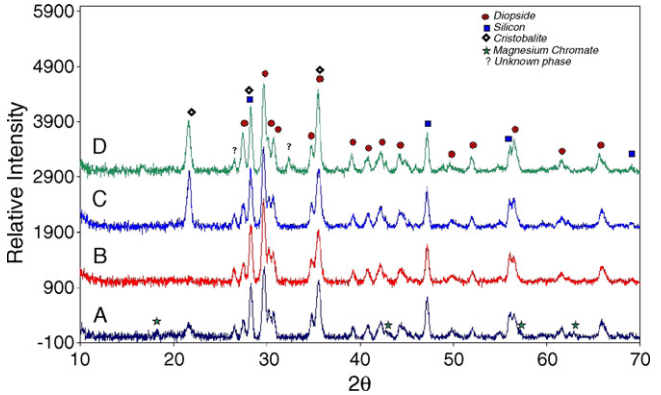

Fig. 3. XRD analysis of prepared glass–ceramics heat treated at their sintering temperatures.

Table 3
Crystalline phases in various samples

Samples	Crystalline phases
A	Diopside–Cristobalite[a]–Magnesium Chromate[a]
B	Diopside
C	Diopside–Cristobalite
D	Diopside–Cristobalite

[a] Minority phases.

which intensified with sintering temperature. This bloating effect arises from reduction of transition metal oxides, presents as nucleator in glasses, which releases of oxygen from the specimens. This phenomenon prevents complete densification of these specimens. Premature crystallization thus necessitates a higher sintering temperature.

Fig. 3 shows X-ray diffraction patterns of the specimens after sintering. With increasing temperature wollastonite disappears, larger amounts of diopside precipitate, and, depending on the firing temperature, extensive crystallization of cristobalite occurs. Table 3 summarizes the existing phases in various samples. The microstructure of sintered glass–ceramics is shown in Fig. 4. As samples C and D were sintered for considerably longer in the crystallization temperatures regime they crystallized more than samples A and B as expected and bigger crystallites are formed. At the lower temperatures at which glasses A and B were sintered, the conditions for nucleation and growth of a new crystalline phase, i.e. cristobalite, and for continuous growth of diopside, are less favorable and microstructures with poor crystallinity appear. In this case, initiation of crystallization from surface of particles inward is observed, as shown in Fig. 4a and b.

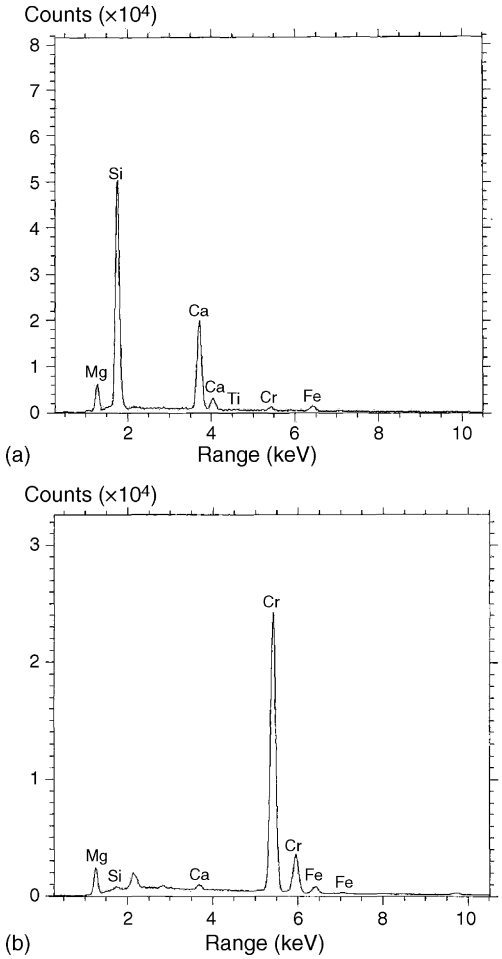

Fig. 5. The EDAX analysis of sample A: (a) diopside, (b) chromium spinel.

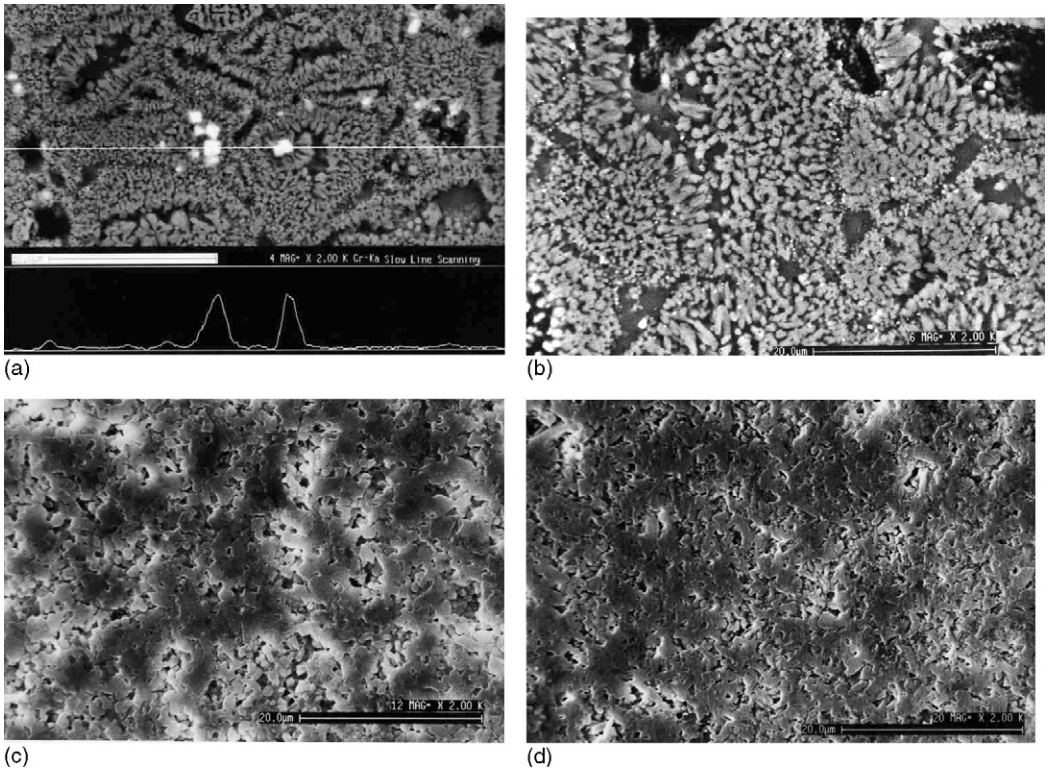

Fig. 4. SEM micrograph of sintered glass–ceramics: (a) sample A, (b) sample B, (c) sample C, (d) sample D.

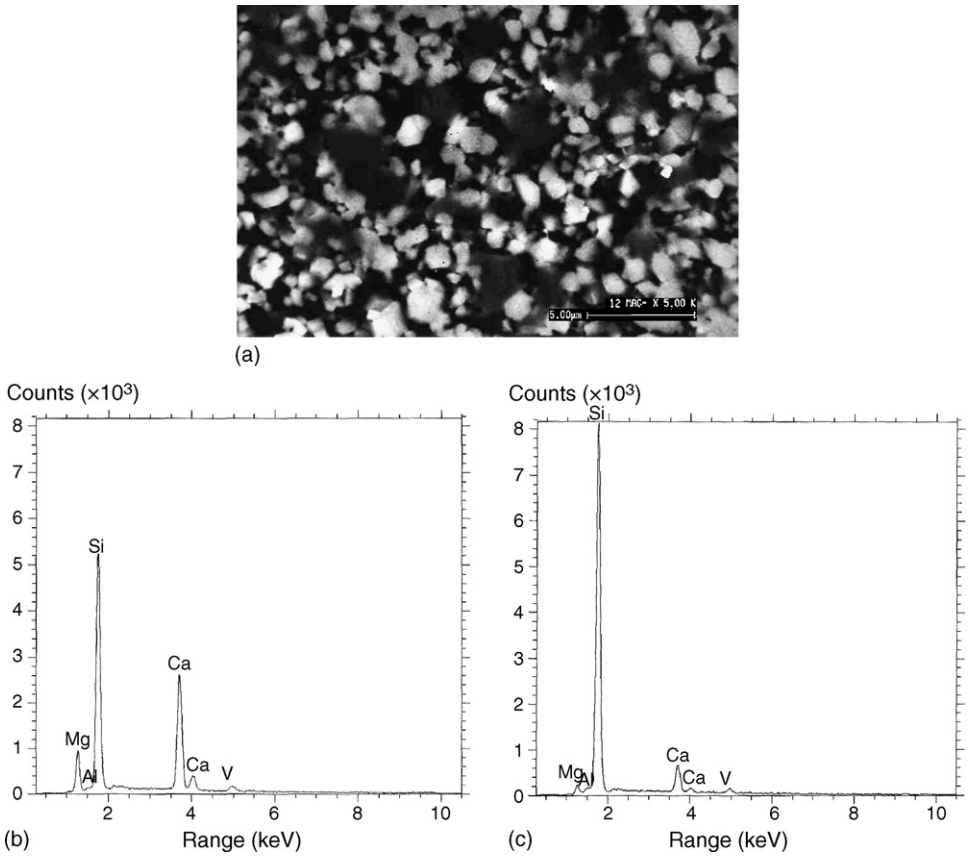

Fig. 6. The SEM micrograph and EDAX analysis of sample C: (a) back scattered micrograph, (b) diopside, (c) cristobalite.

EDAX analysis of the main crystalline phase and of particles appearing lighter in BSE contrast in sample A is shown in Fig. 5a and b. The main precipitated phase is diopside and the lighter one is a chromium spinel phase. The presence of this phase was also detected by the line scan of chrome in the Fig. 4a. Contrary to observations made for the melt-cast method, the spinel phase does not act as an effective nucleating agent and free surfaces of compacted glass particles are more effective sites for nucleation and growth of diopside. The same holds for compound B, in which very bright particles of tungsten compounds can be observed. Fig. 6 shows the BSE micrograph and EDAX analysis of the light and darker crystalline phases of sample C. The chemical composition of the lighter regions is compatible with diopside and the darker with cristobalite.

Bending strength and Vickers microhardness are shown in Table 4. In spite of an almost identical bending strength, the Vickers microhardness falls into two categories, i.e. A and B, C and D, respectively. Presence of micropores and a weaker residual glassy phase, apparently due to presence of V_2O_5, MoO_3 and CaF_2 modifiers are the factors which reduce Vickers microhardness of glass–ceramics C and D considerably.

Table 4
Physical properties of prepared samples

Samples	Bending strength (MPa)	Vickers hardness (GPa)	Relative density (%)
A	82	6.0	96
B	83	7.2	93
C	79	4.6	90
D	89	3.8	92

4. Conclusions

In contrast to the melt-cast method, addition of metal oxides and CaF_2 has no considerable effect on bulk crystallization of the glasses in the SiO_2-CaO-MgO (Na_2O) system prepared by sintering. It is concluded that free surfaces of compacted glass particles are more effective sites for crystallization. The presence of transition metal oxides in glasses causes premature crystallization and necessitates an increase in sintering temperature. Bloating due to reduction of metal oxides prevents complete densification. It was found that, because of their higher crystallization peak temperature, the glass–ceramic containing $Fe_2O_3 + Cr_2O_3$ has desirable sintering behavior and final density.

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