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Study of bulk crystallization in MgO-CaO-SiO_2-Na_2O glasses in the presence of CaF_2 and MoO_3 nucleant

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The crystallization process of MgO-CaO-SiO_2-Na_2O glasses in the presence of CaF_2 and MoO_3 nucleating agents was investigated by DTA, XRD and SEM. The effect of compositional changes on bulk crystallization and growth morphology has been studied. After a two-stage heat treatment, the phases such as wollastonite, diopside and cristobalite, were identified. The ability of CaF_2 and MoO_3 pair as nucleating agents in inducing bulk nucleation in these glasses was attributed to the surface tension and viscosity reductions. The observed pore formation phenomenon upon the increase of MgO content in these glass-ceramics was related to the difference in density between the residual glass and diopside as the main crystalline phase. © *2003 Kluwer Academic Publishers*

1. Introduction

Glass-ceramic materials are polycrystalline solids containing residual glass phase, prepared by melting glass and forming it into products that are subjected to controlled crystallization. The concept of controlled crystallization of glass designates the separation of a crystalline phase from the glassy parent phase in the form of tiny crystals, where the number of crystals, their growth rate and thus also their final size are controlled by suitable heat treatment [1].

Efficient nucleation of crystals from numerous centers within the bulk material and their subsequent growth results in internal crystallization as opposed to surface crystallization in which crystallization initiates at the surface and usually gives rise to a coarse microstructure.

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 homogenously dispersed in the glass volume [2]. It is obvious that internal crystallization will be greatly facilitated by using suitable nucleating agents.

Glass-ceramics obtained from crystallization of glass compositions located in the SiO_2-CaO-MgO and related systems which may contain several phases such as wollastonite, forsterite, diopside, protoenstatite and akermanite. Owing to the peculiar durability and mechanical properties may be suitable for many applications [3].

In resent years also great attention has been paid to the strong and bioactive glass-ceramics with biomedical applications which mainly can be located within these systems [4–6].

Considering the relative difficulty of initiation of internal nucleation and bulk crystallization in glasses of these systems and the fact that some aspects of their devitrification process are still unclear, it was decided to conduct a comprehensive investigation on nucleation and bulk crystallization of these glasses.

The effect of many nucleation agents such as TiO_2, Cr_2O_3, CaF_2, Fe_2O_3, V_2O_5, LiF etc. have been studied in SiO_2-MgO-$CaO(Al_2O_3,R_2O\ldots)$ systems [7–11].

Molybdenum oxide also has successfully been used as crystallization catalyst in Lithia containing glass-ceramics [12].

The effect of $(Cr_2O_3+Fe_2O_3)$ and $(Fe_2O_3+WO_3)$ pairs as nucleating agents have also been reported by the present authors for glasses of SiO_2-CaO-$MgO(Na_2O)$ system [13, 14].

In this work, bulk crystallization of glasses containing SiO_2, MgO, CaO and Na_2O in the presence of CaF_2+MoO_3 nucleant and the effect of compositional changes on the crystallization behavior and microstructure of glass-ceramic products were investigated. Although, CaF_2 and MoO_3 are common nucleating agents, to the authors, knowledge there is no report in the literature on the usage of them as a pair in the crystallization of these glasses.

In the production of glass-ceramic articles, glass shaping is either performed by direct casting of molten glass or by sintering of glass powders. In the latter technique, the fritted glass powder, after being pressed to the desired shape, is consolidated and crystallized by a suitable heat treatment. Owing to the difficulty of initiating bulk nucleation and internal crystallization in these glass-ceramics, the sintering and crystallization method is usually employed, e.g., in the case of bioactive A/W glass-ceramics derived from the above mentioned system [4–6]. In the present work, bulk glass samples were used to study the possibility of initiating effective bulk nucleation and crystallization in this system. Obviously, the bulk crystallization method is of some advantage in comparison to the glass sintering method both economically and from the point of view of microstructural control.

2. Experimental procedure

2.1. Melting and forming

The compositions of glasses and nucleating agents studied are listed in Table I. 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 cast into hot stainless steel moulds. The glasses were annealed at 600°C for 2 h, and then furnace cooled at room temperature.

2.2. Heat treatment procedure

The thermal behavior of glasses was monitored by DTA scans which were carried out using a simultaneous thermal analyzer (Polymer Laboratories, STA-1640). For this purpose, 10 mg of the powder was sieved into fine and coarse fractions (63 and 180–212 μm, respectively) and analyzed against Al_2O_3 powder as the reference material. In the experiment, a heating rate of 10°C min^{-1} in static atmosphere was maintained for all the DTA runs. Each monolithic glass sample then was held at its appropriate nucleation and crystallization temperatures as determined by DTA. In these experiments the heating rate was 5°C min^{-1} up to the nucleation temperature and 1°C min^{-1} between nucleation and crystallization temperatures.

2.3. Microstructural analysis

The Microstructural studies of the glass and the crystallized glass-ceramic, were done by scanning electron microscope (Cambridge, Stereoscan 360). The samples after grinding and polishing were etched in 10% HF for approximately 20 s, and immediately put in an ultrasonic cleaner with warm water for at least 10 min and then were coated with a thin layer of gold. Crystalline phases present in glass-ceramic specimens were identified by X-ray powder diffractometer (Siemens, D-500), using Cu K_α radiation at 40 kV and 30 mA settings in the 2θ range from 5° to 70°. The X-ray diffraction patterns were matched to JCPDS data and corresponding phases were identified.

TABLE I Chemical composition of various glasses (weight percentage)

Sample no.	SiO_2	CaO	MgO	Na_2O	CaF_2	MoO_3
1	59.68	27.25	0	5.08	4.00	4.00
2	59.68	24.23	3.02	5.08	4.00	4.00
3	59.68	21.23	6.02	5.08	4.00	4.00
4	59.68	18.23	9.02	5.08	4.00	4.00
5	59.68	15.23	12.02	5.08	4.00	4.00
6	59.68	12.23	15.02	5.08	4.00	4.00
7	59.68	9.23	18.02	5.08	4.00	4.00
8	59.68	6.23	21.02	5.08	4.00	4.00

3. Results and discussion

3.1. Thermal analysis

In order to evaluate the nucleation mechanisms of the glasses, samples with different specific surface area were studied by DTA. The increase of the specific surface area does not significantly influence the glass transition temperatures, whereas for surface nucleation mechanism, the crystallization peak maxima shift relatively towards lower temperatures. ΔT values are the difference between peak temperatures for two particle size ranges.

At first, CaF_2 and MoO_3 were used singly as nucleating agents in the base glass composition (5.52% Na_2O, 6.54% MgO, 23.08% CaO, 64.8% SiO_2). The ΔT values for samples with 4%wt CaF_2 and MoO_3 were determined as 33° and 30°C, respectively. It was supposed that the use of mentioned nucleants in pair could probably decrease the ΔT value, further and therefore the probability of bulk crystallization could be increased. Therefore a mixture of 4%wt CaF_2 + 4%wt MoO_3 was used as a nucleant in the base glass composition. The ΔT value obtained for this sample was 23°C.

In order to investigate the effect of compositional changes on the ability of bulk crystallization in these glass-ceramics, the content of MgO was increased in the expense of CaO in 3 wt% steps (Table I). The exothermic crystallization peak temperatures for glasses with different compositions and different particle sizes are tabulated in Table II. These results indicate that, the sample no. 2 with 3 wt% MgO shows the lowest ΔT value and highest susceptibility to bulk crystallization. DTA traces shown in Fig. 1 indicate that whereas the samples containing nucleating agents show relatively sharp DTA peaks, the peak intensity of the base

TABLE II Crystallization peak temperatures of two particle sizes for various samples

Sample no.	%MgO	Particle size (μm)	T_p (°C)	ΔT
1	0	<63	860	22
		180–212	882	
2	3.02	<63	827	17
		180–212	844	
3	6.02	<63	866	23
		180–212	889	
4	9.02	<63	856	23
		180–212	879	
5	12.02	<63	850	38
		180–212	888	
6	15.02	<63	867	28
		180–212	895	
7	18.02	<63	856	24
		180–212	880	
8	21.02	<63	865	30
		180–212	895	

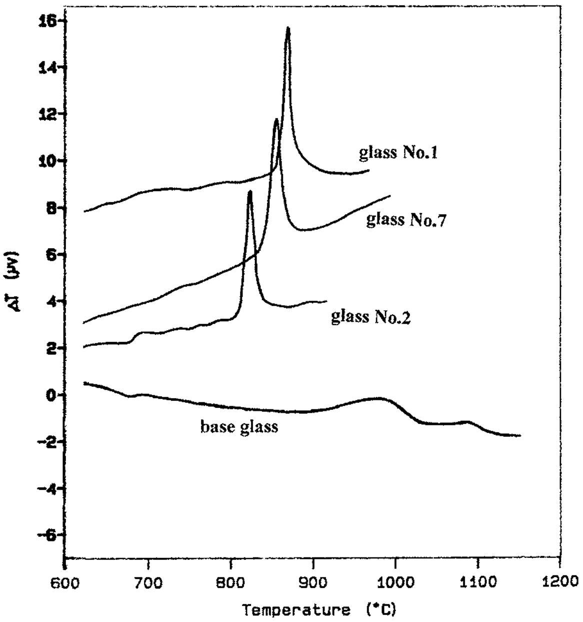

Figure 1 DTA curves for some glass samples with particle size $<63\ \mu$m.

glass (without nucleants) is very low. The intensity of crystallization peak is related to kinetics of nucleation and growth processes during crystallization of glass. The growth rate according to Swift equation is as follows [15]:

$$U = (K/\eta)(T_L - T) \tag{1}$$

where $U =$ The growth rate, K is a constant, $\eta =$ Viscosity of glass, $T_L =$ Liquidus temperature, and $T =$ Crystallization peak temperature.

From Equation 1 it can be seen that the increase in U can be caused by a decrease in η or an increase in T_L value.

It generally is proposed that the introduction of fluorine would result in replacement of the strong Si—O—Si bonds by a pair of much weaker Si—F bonds in the glass structure, causing a reduction in viscosity. The decrease in viscosity positively affects the nucleation and especially growth kinetics [10].

The positive effect of viscosity reduction on the glass nucleation rate could be shown by Equation 2 below:

$$I = \left(\frac{n_v KT}{3\pi\lambda^3\eta}\right)\exp\left(\frac{-\Delta G^*}{KT}\right) \tag{2}$$

where $n_v =$ the number of formula units of the crystallizing component phase per unit volume of melt (glass), $\lambda =$ atomic jump distance, $\eta =$ viscosity of melt (glass), $\Delta G^* = \frac{16\pi\gamma^3 V_m^2}{3(\Delta G_v)^2}$ activation barrier for nucleation (per mole), $V_m =$ molar volume of crystal phase, $\Delta G_v =$ bulk free energy change per mole in crystallization, $\gamma =$ interfacial energy.

Therefore the ability of CaF_2+MoO_3 pair in inducing bulk crystallization in the glasses of this system which is demonstrated itself in relatively low values of ΔT and generally sharp DTA exothermic peaks (compare DTA peaks of the base glass sample with specimen 1 in Fig. 1) can mainly be explained by the great ability of MoO_3 in reducing the glass surface tension [16] and the ability of CaF_2 (or F) in reducing the viscosity of silicate glasses [17]. Surface tension reduction may assists the bulk nucleation process (Equation 2) and lower viscosity promotes both nucleation and growth processes (Equations 1 and 2).

The replacement of CaO by MgO, on the other hand, is a much more complicated process. When calcium is replaced by magnesium, the viscosity is generally first decreases to a minimum, then shows an increasing trend [18], surface tension, on the other hand, is expected to increase by introduction of MgO, since it has the highest factor for surface tension [19]. In Na_2O-CaO-SiO_2 system the introduction of magnesium oxide first decreases the liquidus temperature and crystallization rate, then after a certain minimum, raises the liquidus temperature and intensifies the crystallization process [20].

Therefore the crystallization behavior of specimens no. 1–8 in this work may be explained by the above mentioned (and sometimes contradictory) factors. In the case of specimen no. 2, showing the lowest ΔT value, it seems that the reduction of viscosity owing to the addition of MgO (compare the softening points of specimens 1 and 2 shown on Table IV) is the prevailing factor in promotion of bulk crystallization. The sample no.5 which shows the worse bulk crystallization ability, (judged by its highest value of ΔT), on the other hand, in spite of having a relatively low viscosity (low softening point, Table IV) probability has had a much lower value of liquidus temperature (a lower value of $(T_L - T)$ in Equation 1.

For estimation of maximum nucleation rate temperatures, the samples were first held for 2 h at different nucleation temperatures in 20°C intervals from T_g (glass transition temperature) to T_g+100°C. The degree of crystallization peak shifts to lower temperatures were then measured by DTA for these samples. The greatest shift of the crystallization peak indicates the optimum nucleation temperature [21, 22]. In this way, the temperatures of maximum nucleation and growth rates for bulk samples were found to be 670–690°C and 920–940°C, respectively.

3.2. XRD analysis

After the determination of suitable nucleation and growth temperatures, the samples were held at each given temperature for 3 h. The crystalline phases developed in each sample after the heat treatment process as determined by XRD are tabulated in Table III. Wollastonite, diopside and cristobalite are the major phases existing in the samples. By increasing the MgO content

TABLE III X-ray diffraction results for the heat treated glass-ceramics

Sample no.	Crystalline phases
1	Wollastonite-cristobalite
2	Wollastonite-cristobalite
3	Wollastonite-diopside-cristobalite
4	Diopside-wollastonite[a]-cristobalite
5	Diopside-wollastonite[a]-cristobalite
6	Diopside-cristobalite
7	Diopside-cristobalite

[a] Phases present in minor amounts.

at the expense of CaO, as expected, the peak intensity of wollastonite decreases while the peak intensity of diopside phase increases.

3.3. Microscopic examinations (SEM)

The microstructures of some glass-ceramics are shown in Figs 2–4. It can be seen that the glass-ceramic of composition no. 1 exhibits a fine microstructure comprising tiny crystals of wollastonite with an average dimension of 1–2 μm [Fig. 2]. This indicates the occurrence of an effective bulk nucleation with a relatively slow growth rate, in these specimens.

Fig. 3 shows the microstructure of glass-ceramic no. 2, revealing a much faster and more directional growth of wollastonite crystals. The reduction of viscosity due to the addition of MgO as discussed before may be responsible for faster growth rates in these specimens.

Fig. 4, exhibiting the microstructure of specimen no.7, shows the greater tendency of diopside crystals towards dendritic growth. The much coarser microstructure of specimen no. 7, despite its relatively high viscosity (Table IV), can probably be attributed to the greater value of $(T_L - T)$, higher liquidus temperature (Equation 1) and/or slower nucleation rate owing to the increase of interfacial energy (as a result of replacement of MgO for CaO as discussed before).

In spite of high crystallization ability of glass-ceramics containing $CaF_2 + MoO_3$ the existence of considerable porosity in some of the glass-ceramics, especially those with high percentage of MgO, is undesirable. Millimeter sized pores were observed in some cases, e.g. sample no. 7.

The observation of porosity when diopside phase is formed, was reported by other investigators. Agarwal *et al.* [23] believed that the evolution of a gas from the residual glassy phase caused the pore formation. If the

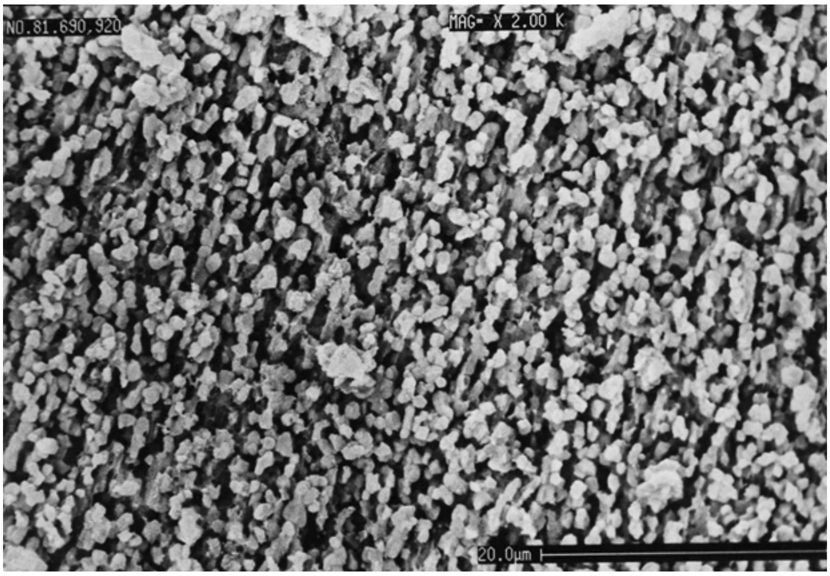

Figure 2 SEM micrograph of glass-ceramic no.1, heat treated: 3 h at 680°C, 3 h at 920°C.

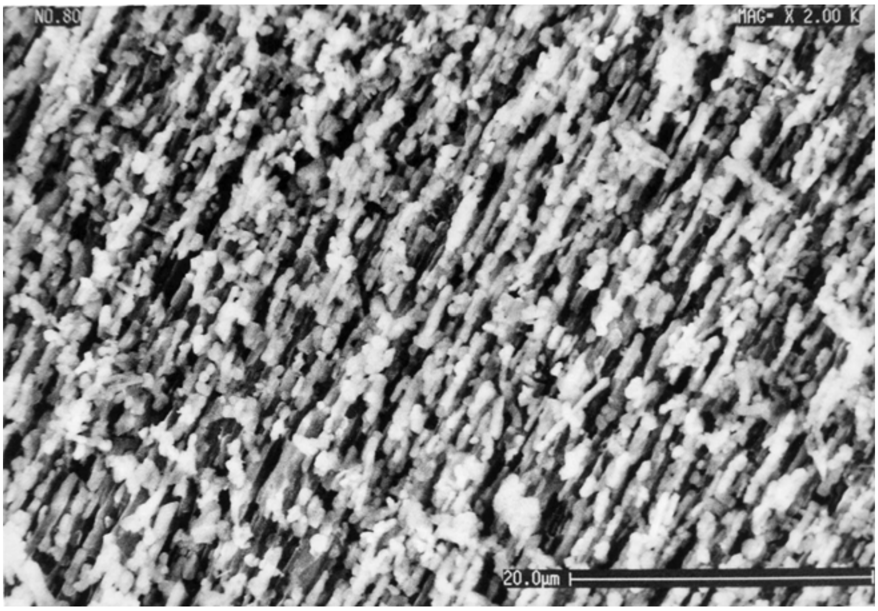

Figure 3 SEM micrograph of glass-ceramic no. 2, heat treated: 3 h at 670°C, 3 h at 920°C.

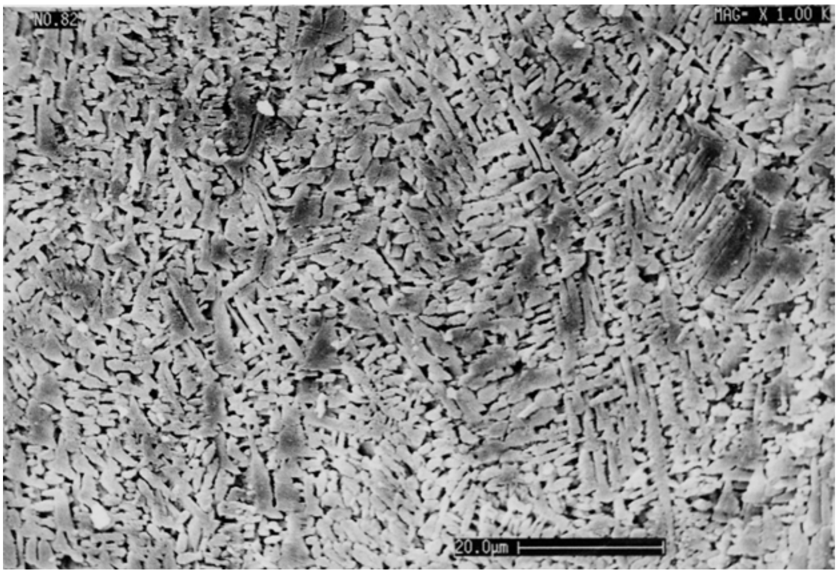

Figure 4 SEM micrograph of glass-ceramic no. 7, heat treated: 3 h at 680°C, 3 h at 940°C.

above theory was correct, then the following mechanisms may be operative:

1. Lower solubility of gases in the diopside phase in comparison to the parent glass. This would result in the increase of dissolved gases in the glass phase. The consumption of MgO, on the other hand, may give rise to a decrease in surface tension of residual glass and facilitates the gas nucleation and formation of bubbles in the glassy phase.
2. A preferential gas bubble nucleation may occur at the diopside-glass interface.

In order to verify the accuracy of the above theories, the raw materials of the samples were calcined first at 400°C and then at 1000°C for 6 h, as usual prior to the performance of final melting and heat treating processes.

The specimens again contained the same amount of porosity with almost the same mean size. Therefore it seems that the theory of pore formation according to Agarwal *et al.* [23] is not operative in this case.

Our density measurements indicated that the densities of glass-ceramics were much higher than the parent glass in these samples (e.g., the densities of glass sample no.7 and its glass-ceramic counterpart were found to be 2.63 and 3.35 g/cm^3 respectively). The densities of diopside and wollastonite are 3.39 and 2.86 g/cm^3 respectively. Therefore it is expected that those glass-ceramics containing diopside as the major crystalline phase are generally more susceptible to pore formation owing to the density differences between crystalline phases and glassy residue.

TABLE IV Dilatometric softening points of various glass samples

Sample no.	Softening point (°C)
1	737
2	670
4	673
5	673
6	683
7	709
8	746

Marghussian and Niaki [24] also have reported the formation of pores during crystallization of diopside phase in some glass-ceramic specimens. They attributed this to the existence of considerable difference between densities of glassy and crystalline phases. According to these investigators the porosity is mainly formed at the final stage of crystallization. At this stage the lack of sufficient glassy phase to fill the gaps resulting from crystallization (due to a difference between densities of glassy and crystalline phases) leads to formation of some porosity.

In some specimens containing low percentages of MgO (e.g., specimen no. 2) some cracks were observed at the surface of specimens after heat treatment. These cracks may be due to the presence of cristobalite in these glass-ceramics. The volume changes accompanying the phase transition of cristobalite and existing differences between the linear coefficients of thermal expansion of different phases may be responsible for this. The thermal expansion of diopside, wollastonite and cristobalite are 5.0×10^{-6}, 9.4×10^{-6} and 27×10^{-6}/°C (20–600°C) respectively [25].

4. Conclusions

1. It seems that the simultaneous use of CaF_2 and MoO_3 nucleants has a positive role in inducing bulk crystallization in the specimens, investigated herein. The addition of CaF_2 and MoO_3 causes a decrease in viscosity and surface tension respectively, facilitating the nucleation and growth processes.
2. The major phases after heat treatment of glasses were wollastonite, diopside (>6 wt% MgO) and in some cases cristobalite.
3. Increasing the magnesium oxide content in this group of glass-ceramics, generally results in faster growth rates, coarser microstructures and dendritic morphology of crystals, especially in specimens with diopside as their dominant, major phase.

4. Addition of MgO above a certain level may cause a considerable pore formation in the glass-ceramic specimens. This phenomenon could be related to diopside formation and the difference in density existing between it and the residual glassy phase.

5. Formation of cristobalite in some specimens may cause cracking due to the volume changes accompanying the phase changes of cristobalite. This phenomenon is more distinct in specimens containing lower amounts of MgO.

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