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The effect of TiO_2 on phase separation and crystallization of glass-ceramics in $CaO–MgO–Al_2O_3–SiO_2–Na_2O$ system

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The experiments were carried out on studying the effect of phase separation on nucleation and crystallization in the glass based on the system of $CaO–MgO–Al_2O_3–SiO_2–Na_2O$. In the experiments, TiO_2 was chosen as nucleating agent. Three batches of 5, 8 and 10 wt% TiO_2 substitution were investigated by the techniques of DSC, XRD, FTIR and FESEM equipped with EDS. XRD and FTIR analysis indicated that the super cooled glasses were all amorphous, the heat treatment leading to nucleation would cause a disruption of silica network which followed phase separation. The phase separation followed the generation of crystal seeds $Mg(Ti,Al)_2O_6$. FESEM observation and EDS analysis revealed that the more TiO_2 content of glass, the more droplet separated phase and crystal seeds after nucleation heat treatment. The main crystal phase is clinopyroxene, $Ca(Ti,Mg,Al)(Al,Si)O_6$, of crystallized glass.

1. Introduction

Glass-ceramics are polycrystalline materials produced by controlled crystallization of glasses [1]. There is a two-stage heat treatment in controlling crystallization, namely a nucleation and crystallization stage [2]. The key stage is the former one, in which small nuclei are formed within the parent glass. There are two different styles of nucleation, homogeneous and heterogeneous ones [3]. Generally, the heterogeneous nucleation means that the nuclei formed in the glass with some so-called nucleating agents added.

Prior to the formation of nuclei, there is a process of units' transmission and transforming in glass; totally we could call this process phase separation [4]. In certain conditions, phase separation could promote the nucleation and crystallization. Several studies have been performed to evaluate the effects of phase separation on nucleation and crystallization with the nucleation agents added. Uhlmann and co-workers [5] suggested that the nucleation agents could be selectively enriched in one separated phase thus provide the cites for nucleus. McMillan [6] argued that some metal oxides, such as P_2O_5, MoO_3, WO_3, could also be the agents in silicate glasses and so on. In a recent study, Shen et al. [7] reported that Cr_2O_3 could promote glass phase separation and be enriched in one phase in $CaO–MgO–Al_2O_3–SiO_2$ system glass, and Cr_2O_3 would facilitate nucleating heterogeneously in the enriched phase. However, to the authors' knowledge, the effect of TiO_2 as this type of agent in silicate glass has not been well evaluated. This paper summarizes the results of a study concerning the role of TiO_2 in the process of phase separation, nucleation and crystallization of $CaO–MgO–Al_2O_3–SiO_2–Na_2O$ system glass.

2. Experimental

2.1. Preparation of glasses and thermal processing

High-purity silica sand, alumina, reagent grade chemicals of CaO, MgO, Na_2CO_3 and TiO_2 were used as raw materials for glass preparation. Three prepared glasses of different compositions are termed as A, B and C. Table 1 presents the chemical compositions of each glass, it can be seen that TiO_2 is incorporated as a substitution in each one.

Three batches of various composition of these materials totaled 50 g were prepared and each batch of such materials was mixed thoroughly. They were melted in 100 ml corundum crucibles (99 wt% Al_2O_3 purity) at 1500 °C for 3 h in an electric furnace in air. The molten was then poured into preheated saggars and annealed at 550 °C for 30 min. They were then cooled to room temperature. Approximately 1 g of each glass was quenched in water and dried in dry box. It was further grounded into a fine particle sizes for the DSC (differential scanning calorimetric) measurement.

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Table 1
Compositions of the prepared glasses (wt%)

Oxide	Glass		
	A	B	C
SiO_2	56.6	54.7	53.6
Al_2O_3	6.4	6.2	6.1
MgO	3.2	3.1	3.1
CaO	25.7	24.9	24.5
Na_2O	3.1	3.0	2.9
TiO_2	5	8	10
Total	100	100	100

Table 2
T_g and T_c of each glass (°C)

	Glass		
	A	B	C
T_g	735	735	733
T_c	972	956	928

The glasses were then heat-treated at a temperature 50 °C higher than T_g for 30–120 min for the purpose of observation of phase separation behavior by FESEM (field emission scanning electron microscope) method. They were subsequently further heat-treated under various conditions for crystallization studies.

2.2. Techniques for characterization

Glass transition temperature (T_g), crystallization exothermal temperature (T_c) were measured by using a DSC (STA 409C/CD Netzsch Gerätebau GmbH, selb, Germany), operating at 10 °C/min heating rate from room temperature to 1100 °C in air.

The X-ray diffraction (XRD) spectra of the fine powdered glasses were recorded with a Mac M21X diffractometer. The Cu kα radiation ($\lambda = 0.15405$ μm) with Ni filter and 0.1 mm detector was used at 50 kV and 40 mA. X-ray patterns were gathered in the range 10–65° 2θ with a step size of 0.02° and a step time of 5 s.

The fine structure of glasses and glass-ceramics were observed with a SUPRA™55 field emission scanning electron microscope (FESEM) equipped with an energy dispersive spectrometer (EDS). The fractured surface of the glass was etched in 1% HF solution for 30 s at room temperature for FESEM observation.

Infrared spectra were recorded between wavenumber 400 and 4000 cm^{-1} with a Nicolet Avatar 360 FTIR spectrometer.

3. Results

3.1. DSC measurement

The glass transition temperatures (T_g) and the exothermal troughs temperatures (also known as the crystallization temperature, T_c) of these three glasses were recorded by DSC curves shown in Fig. 1, and the values of T_g and T_c are presented in Table 2. The glass transition temperature of glass A is only 2 °C less than the other two, but, for T_c measurements there are obvious differences, the lowest one is 928 °C for glass C, 956 °C for B, while for glass A is 972 °C. The content of TiO_2 was significant.

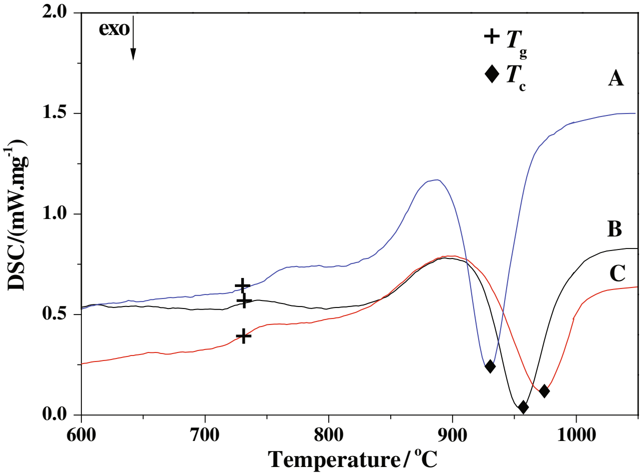

Fig. 1. DSC curves of three glasses.

A heat treatment for each glass was carried out at a temperature of 785 °C which was 50 °C higher than its T_g, and the time was 120 min. The nucleated glasses were then heat treated for crystallization at T_c for a period of time.

3.2. XRD analysis

Fig. 2 represents the XRD patterns of annealed glasses. It can be seen that there is none crystal peak on each pattern. It revealed that three annealed glasses had not devitrified during the cooling process.

Fig. 3 shows the TiO_2 content dependence of XRD patterns of nucleated glasses. XRD investigation reveals that the main crystalline phase is clinopyroxene, $Ca(Ti,Mg,Al)(Al,Si)O_6$ for the glass C (Fig. 3, pattern C); some clinopyroxene and quandilite crystal seeds

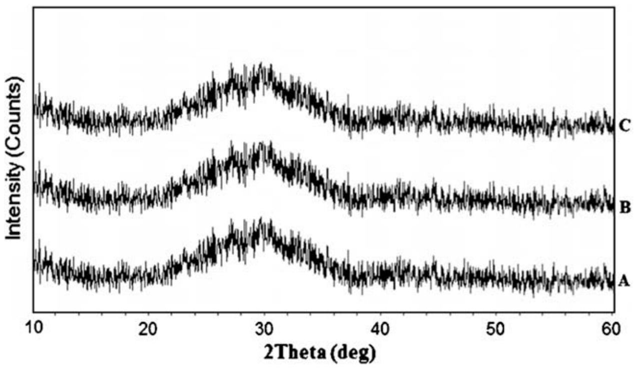

Fig. 2. XRD patterns of annealed glasses.

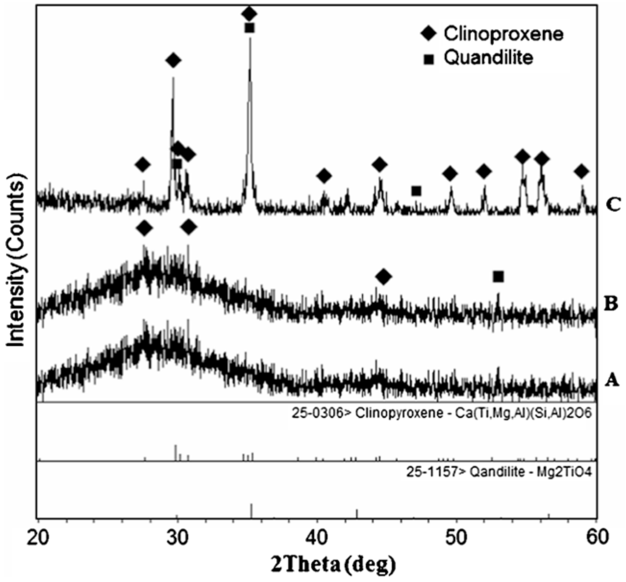

Fig. 3. XRD patterns of nucleated glasses.