



Effects of alkali metal oxides on crystallization behavior and acid corrosion resistance of cordierite-based glass-ceramics



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ABSTRACT

MgO-Al₂O₃-SiO₂-TiO₂ glass-ceramics with 3 mol% alkali metal oxides were prepared, and the 3 mol% alkali metal oxides were induced by 3 mol% Na₂O only, 1.5 mol% Na₂O + 1.5 mol% Li₂O, and 1.5 mol% Na₂O + 1.5 mol% K₂O, respectively. Effects of alkali metal oxides on the crystallization behavior and acid corrosion resistance of the MgO-Al₂O₃-SiO₂-TiO₂ glass-ceramics were investigated. The results showed that μ-cordierite precipitated in the glass matrix firstly, and it changed into α-cordierite with the crystallization temperature increasing. Using K₂O substitution of Na₂O hindered the precipitation of cordierite, while the addition of Li₂O promoted the precipitation of μ-cordierite at low temperatures. When the main crystalline phase was μ-cordierite, the acid resistance of the glass-ceramics was significantly improved compared with the base glass. With the main crystalline phase changing from μ-cordierite to α-cordierite, the acid resistance of the glass-ceramics became worse, which was related to the honeycomb structure of α-cordierite. When 1.5 mol% Na₂O was replaced by Li₂O, the glass samples crystallized at 880 °C showed the optimum acid resistance with the minimum weight loss ~0.096%.

1. Introduction

Cordierite (Mg₂Al₄Si₅O₁₈) based MgO-Al₂O₃-SiO₂ (MAS) glass-ceramics have many beneficial properties, such as low dielectric constant, low thermal expansion coefficient, good mechanical and chemical properties [1,2]. Due to their outstanding properties, cordierite based glass-ceramics have wide applications in the fields of high voltage and high vacuum [3], microelectronic packaging [4,5] and glazes for floor tiles [6,7]. As is well known, cordierite has three polymorphic forms [8,9]: μ-cordierite (a metastable form with β-quartz structure), β-cordierite (a stable low-temperature form) and α-cordierite (a stable high-temperature form). The study shows that the α-cordierite and μ-cordierite usually co-existed in the glass-ceramics in which the μ-cordierite crystals occur as the initial crystalline phase, followed by its transformation at higher temperatures to the α-cordierite phase [10–13]. It is necessary to control the precipitation of μ-cordierite, which would worsen the thermal and dielectric properties of the glass-ceramics [9,14,15].

In addition, the high concentrations of SiO₂ and Al₂O₃ in MAS

glasses result in high melting temperatures and viscosities, which make them difficult to be prepared [10,16]. So fluxes are introduced to reduce the viscosity and melting temperature, meanwhile, they may run parallel to change the crystallization behaviors and properties [17]. Chen [5] found that ZnO could decrease the batch melting temperature, glass transition temperature and crystallization temperature of cordierite-based glass-ceramics. Torres and Alarcon [6] pointed out that B₂O₃ as flux in the cordierite primary phase field of the CaO-MgO-Al₂O₃-SiO₂ quaternary system favored the crystallization of α-cordierite as the only crystalline phase. As the most commonly used fluxes, alkali oxides have been introduced to reduce the viscosity and the melting temperature. However, the effect of alkali oxides on cordierite phase transition and chemical properties, especially acid resistance, has rarely been reported.

Thereby, the objectives of this work are to focus on the effect of alkali metal oxides on the phase transformation, crystallization kinetics and acid resistance of cordierite-based glass-ceramics, in order to broaden its applications in other fields.

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Table 1
Compositions of base glasses (mol%).

Samples	MgO	Al ₂ O ₃	SiO ₂	TiO ₂	Li ₂ O	Na ₂ O	K ₂ O
S1	15	15	60	7	–	3	–
S2	15	15	60	7	1.5	1.5	–
S3	15	15	60	7	0	1.5	1.5

2. Experimental

2.1. Glass prepared

The parent glasses were prepared from analytical grade SiO₂, Al₂O₃, MgO, TiO₂, Na₂CO₃, Li₂CO₃ and K₂CO₃. TiO₂ was used as the nucleating agents to promote the bulk crystallization [1,8,18]. The detailed chemical compositions were shown in Table 1. The glass batch was melted in the platinum crucible in electrical furnace at 1550–1580 °C for 3 h. And the glass melt was quenched onto a preheated steel mold and then annealed at about 20 °C lower than their glass transition temperatures.

2.2. Characterizations

To estimate the crystallization mechanism and determine the heat-treat schedules, the glass powders were measured by DSC method (Netzsch STA 409, German) in air atmosphere at the heating rate of 5, 10, 15 and 20 °C/min from 20 to 1200 °C respectively, using Al₂O₃ as reference material. The platinum crucible was used in the DSC tests. Air flow rate through the sample pan was kept constant at 50 mL min⁻¹. The glass-ceramic specimens were crushed and milled into powder to analyze the crystalline phase through X-ray diffraction (XRD, D/max-RB 2500 V, Rigaku, Japan). The CuK_α radiation ($\lambda = 0.15405 \mu\text{m}$) was used at 40 kV and 40 mA. The diffraction patterns were recorded in the 2θ range from 10 to 70° at a scan rate of 2° min⁻¹. The powders of the glass-ceramics (particle size: 0.5 mm ~ 1.0 mm) were etched in 20 mol% H₂SO₄ solution at 95 °C for different duration and the chemical resistance was evaluated by the weight loss percentage: $(m_0 - m_1) / m_0 \times 100\%$, where m_0 and m_1 were the weights of the samples before and after corrosion, respectively. The surface of the bulk samples etched by 20 mol% H₂SO₄ solution was observed via field emission–environment scanning electron microscope (FE-SEM, Hitachi S-4800 model, Japan) and energy dispersive spectroscopy (EDS). Five samples for each area were used to calculate the average value regarded as the final value.

XPS analysis was conducted using an ESCALAB250Xi (Thermo Scientific, UK) spectrometer with a monochromatic Al K_α radiation source operating at 300 W. During analysis vacuum was maintained < 10⁻⁹ mbar. All the absolute binding energies of the photoelectron spectra were referenced to the monitored C_{1s} signal at 284.6 eV. The O_{1s} photoelectron spectra were fitted with a 30% Gaussian–70% Lorentzian function. A non-linear, least square fitting algorithm was used to find each best fit solution.

3. Results and discussion

3.1. Crystallization behavior of MAS glass-ceramics

Fig. 1 showed the DSC curves of the MAS glasses with different alkali metal oxides. The glass transition temperatures (T_g) of sample S1, S2 and S3 were 746, 741 and 763 °C, respectively. When 1.5 mol% Na₂O was replaced by Li₂O, the T_g of the glasses decreased. However, when 1.5 mol% K₂O substituted for Na₂O, the T_g increased. Alkali metal oxides were common flux in glasses, which can provide free oxygen in the glass network and decrease the viscosity. The distributions of [SiO₄] structural units Q_n , where n is the number of bridging oxygen atoms

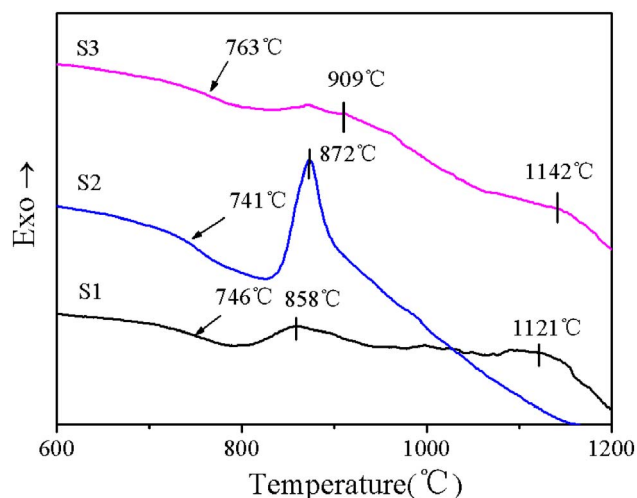


Fig. 1. DSC curves of glass samples.

bonded to other Si atoms, were affected by the alkali oxides obviously. The reaction, $2Q_n = Q_{n-1} + Q_{n+1}$ ($n = 3, 2, 1$), proceeds to the right direction as the field strength of R^+ ions (Z/r) increases ($Li^+ > Na^+ > K^+$) at the same R^+ concentration [19]. It was associated with the T_g decreasing degree in the order: $Li^+ > Na^+ > K^+$ [20].

The DSC curves of S1 and S3 both have two broader crystallization peaks around 900 and 1100 °C, while the curve of S2 presents only one but sharp crystallization peak at 872 °C, which reveals higher crystallization rate. According to the DSC traces, all specimens were nucleated at 30–50 °C above their T_g for 2 h and then crystallized at the temperature ranges from 880 to 1200 °C for 2 h.

The glass S1 was nucleated at 780 °C for 2 h and then crystallized at 880, 1000, 1100, 1150 and 1200 °C for 2 h, respectively. The powder XRD patterns of glass-ceramics with different heat treatments were shown in the Fig. 2. When crystallized at 880 °C, the sample was still almost amorphous phase, and only small amount of μ -cordierite ($Mg_2Al_4Si_5O_{18}$; JCPDF no.14-0249) appeared, which is a kind of β -quartz solid solution ($2Al^{3+} + Mg^{2+} = 2Si^{4+}$) [18]. When the crystallization temperature increased to 1000 °C, the diffraction peaks intensity of μ -cordierite increased and sapphirine ($Mg_2Al_4SiO_{10}$; JCPDF no. 19–0750) occurred in the glass matrix. When the glass sample S1 crystallized at 1100 and 1150 °C, the peak intensities of μ -cordierite and sapphirine crystalline phases both increased. With the crystallization

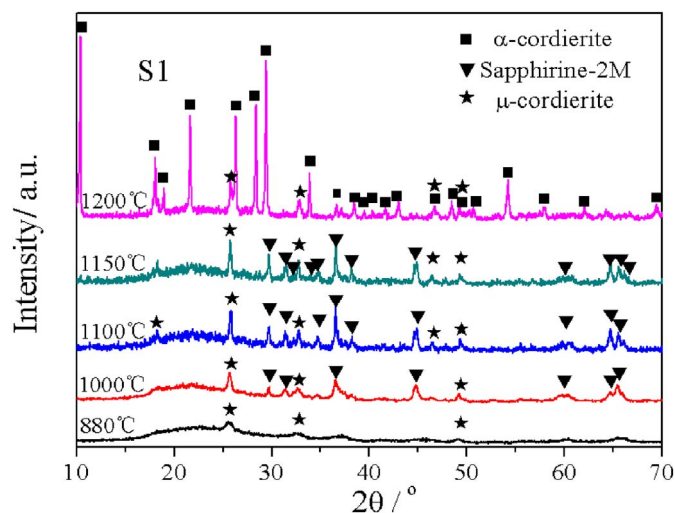


Fig. 2. XRD results of glass S1 after two step heat-treatments.

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