



Effect of molybdenum and titanium oxides on mechanical and thermal properties of cordierite–enstatite glass-ceramics



Kei Maeda ^{a,*}, Yoichi Sera ^a, Atsuo Yasumori ^b

^a Asahi Glass Co., Ltd., Research Center, 1150 Hazawa-cho, Kanagawa-ku, Yokohama 221-8755, Japan

^b Tokyo University of Science, Department of Materials Science and Technology, Japan

ARTICLE INFO

Article history:

Received 7 October 2015

Received in revised form 10 November 2015

Accepted 12 December 2015

Available online xxxx

Keywords:

Glass-ceramics

Cordierite

Enstatite

Molybdenum

ABSTRACT

By adding either MoO₃ or TiO₂ as nucleating agents, glass at the eutectic point of cordierite (2MgO·2Al₂O₃·5SiO₂) and enstatite (MgSiO₃) in the MgO–Al₂O₃–SiO₂ ternary system was crystallized. Although bulk crystallization required adding 10 wt% TiO₂, approximately 0.1–0.5 wt% of MoO₃ induced bulk nucleation when the parent glass was melted under reducing conditions. For both TiO₂- and MoO₃-nucleated glasses, the glass-ceramics containing both cordierite–enstatite as main crystalline phases were obtained by heat-treatment at 1200 °C. The fracture toughness of the glass-ceramics nucleated by TiO₂ was 1.5 times higher than that of sintered cordierite ceramics. In addition to two main crystalline phases, magnesium titanium oxide and rutile also precipitated in TiO₂-nucleated glass. The additional effects of TiO₂ on the properties of the glass-ceramics were identified by comparing the TiO₂- nucleated glass-ceramics and MoO₃- nucleated one. The addition of TiO₂ slightly increased the Young's modulus of the glass-ceramics. On the other hand, since TiO₂ suppressed the precipitation of enstatite, the thermal deformation of TiO₂-nucleated glass-ceramic at 1100 °C was larger than that of MoO₃-nucleated one. Therefore, MoO₃ is the preferable nucleating agent of the glass-ceramics for application which requires high thermal endurance.

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1. Introduction

Glass-ceramics have found many industrial applications, including as cooking ware [1,2], cooktops [1,2], heat-resistant windows for stoves or furnaces [1,2], building walls [2,3], and magnetic disk substrates [4]. Recently, new applications of glass-ceramics have also been proposed such as for the components of portable electronic devices [5]. The glass-ceramic Li₂O–Al₂O₃–SiO₂ (LAS) system, which precipitates from β-quartz solid solutions or β-spodumene (Li₂O·Al₂O₃·6SiO₂), is a commercially important glass-ceramic material because of its low thermal expansion and transparency for some specific uses [1,2]. Glass-ceramics in the MgO–Al₂O₃–SiO₂ (MAS) system have also been studied and applied to industrial uses. Cordierite (2MgO·2Al₂O₃·5SiO₂) is one of the most important constituents of MAS glass-ceramics because it has low thermal expansion and is highly refractory. It also has superior electrical properties, such as a low dielectric loss. These superior characteristics of cordierite have attracted significant research efforts in cordierite-containing glass-ceramics. The first commercially successful product involving cordierite glass-ceramics was “Pyroceram” (Corning 9606), which was designed in the 1960s for missile radomes [1,2,6]. In the 1980s, glass-ceramic substrates were studied for use in electrical applications as substitutes for alumina substrates [7]. In recent years,

cordierite glass-ceramics doped with NiO were investigated for applications involving infrared radiation [8]. Most recently, cordierite–enstatite families of glass-ceramics were proposed for use as substrates for GaN in light-emitting diodes, since those have good thermal stability (to 1100 °C), as well as good thermal expansion matching with GaN [9]. With a fracture toughness of 5 MPa m^{1/2}, enstatite (MgSiO₃) is also as one of the toughest glass-ceramics known [10]. Although some of the MAS glass-ceramics mentioned above are made by sintering glass powders [7], bulk-crystallized glass-ceramics still attract significant interest because their parent glass is easy to form by pressing or drawing techniques.

For both cordierite and enstatite, TiO₂ and/or ZrO₂ are often used as nucleating agents for the bulk crystallization of MAS glass-ceramics. The process of nucleation via cordierite or enstatite has been studied extensively [11–13]. Recently, a new approach involving the X-ray absorption near edge structure technique has been used to investigate the nucleation kinetics of MAS glass doped with TiO₂ [14] and ZrO₂ [15]. Such sustained research into MAS glass-ceramics testifies to the significant long-term scientific and industrial interests that these materials have attracted.

One of the issues for glass-ceramics involves conventional nucleating agents, such as TiO₂ and ZrO₂, is that those are required several wt% [1,6,9–12] for sufficient nucleation of the glass. These agents not only provide nucleating sites for the main crystalline phases but also precipitate themselves in crystalline form in the final material. These

* Corresponding author.

E-mail address: kei-maeda@agc.com (K. Maeda).

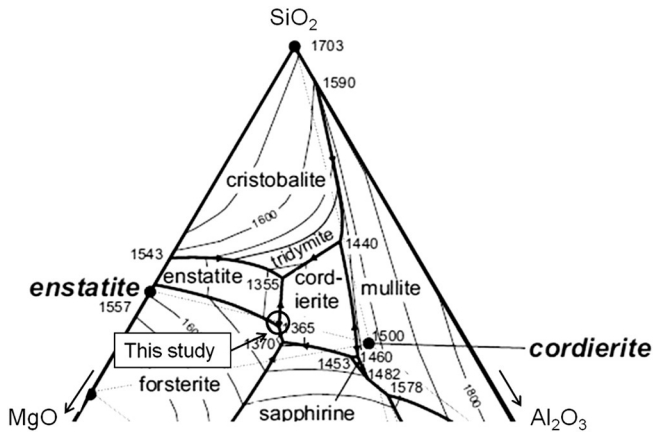


Fig. 1. Phase diagram of MAS [18] showing the glass composition of the present study.

agents are thus expected to affect the microstructure of the resulting glass-ceramics, and therefore, they are likewise expected to have non-negligible effects on the physical properties of the final product. Unfortunately, identifying these effects has proven to be difficult because the bulk crystalline material in MAS systems is hard to obtain without using such nucleating agents. In a recent study that addressed this question, we found that 0.5 wt% of MoO_3 is required to obtain bulk crystallization in MAS glass when the parent glasses were melted in reducing condition [16]. In the present work, to better understand the phase transition and other physical properties of glass-ceramics, we further exploit this phenomenon by comparing MoO_3 -nucleated glass-ceramics with glass-ceramics nucleated by conventional nucleating agents.

For some applications of the glass-ceramics, the thermal endurance of the material plays an important role [9,17]. Since less residual glassy phase (high crystallinity) is preferable for this purpose, the parent glass composition should be close to stoichiometric composition of the crystalline phase, i.e., cordierite in MAS glass (Fig. 1). However, in that cases the glass composition shows high liquidus temperature that is undesirable for good glass formability.

For the present work, we use the glass composition of $55\text{SiO}_2\text{--}20\text{Al}_2\text{O}_3\text{--}25\text{MgO}$ (wt%), which is close to the eutectic point between cordierite and enstatite (i.e., 57.3 wt% cordierite + 42.7 wt% enstatite; see Fig. 1 [18]) to ensure low liquidus temperature. In addition, if both cordierite and enstatite precipitate from the glass, the glass can, theoretically, become 100% crystalline. The glasses in this study were nucleated by either TiO_2 or MoO_3 and crystallized. The creep behavior was evaluated at high temperature for both TiO_2 - and MoO_3 -nucleated glass-ceramics. Density, thermal expansion coefficient, Young's modulus, and fracture toughness of these glass-ceramics were also measured. The crystallization process and microstructures of the glass-ceramics were examined to understand the effect of these nucleating agents.

Table 1
Glass compositions and melting conditions used in this study.

Sample	A		B		C		D		E		F	
	wt%	mol%	wt%	mol%	wt%	mol%	wt%	mol%	wt%	mol%	wt%	mol%
Glass composition												
SiO_2	52.4	51.0	51.1	50.2	50.0	49.3	54.9	52.9	54.9	52.9	54.7	52.9
Al_2O_3	19.0	10.9	18.6	10.7	18.2	10.6	20.0	11.3	20.0	11.3	19.9	11.3
MgO	23.8	34.6	23.3	34.0	22.7	33.4	25.0	35.8	24.9	35.8	24.9	35.7
TiO_2	4.8	3.5	7.0	5.1	9.1	6.7						
MoO_3							0.1	0.04	0.2	0.08	0.5	0.2
Total	100	100	100	100	100	100	100	100.04	100	100.08	100	100.2
Melting temperature (°C)	1550		1550		1550		1550		1550		1550	
Melting Atmosphere	Air		Air		Air		Gas burner*		Gas burner*		Gas burner*	

* Oxygen concentration < 1%.

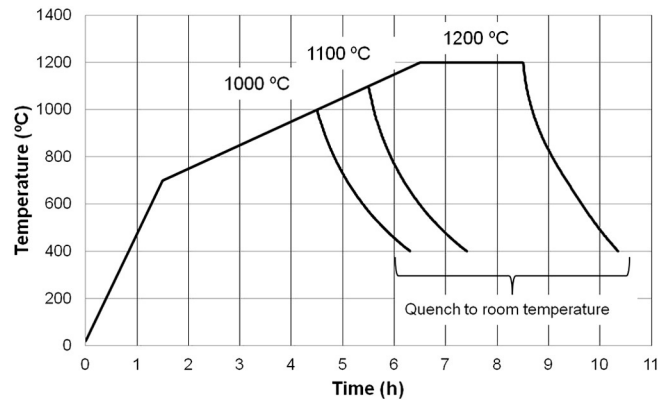


Fig. 2. Heat treatment for crystallization of glasses.

2. Experiment

2.1. Preparation of parent glasses

The samples of parent glass were prepared by the conventional laboratory-scale melting method. The nucleating agents comprised 5, 7.5, and 10 wt% TiO_2 or 0.1, 0.2, and 0.5 wt% MoO_3 . Glass melts (300 g) were obtained from reagent-grade SiO_2 , Al_2O_3 , MgO, TiO_2 , or MoO_3 as starting materials. For glass containing MoO_3 , 0.1 wt% of carbon powder was mixed into the glass batches, which were then melted under a reducing atmosphere (oxygen concentration below 1%) by introducing a town gas burner flame into the electric furnace. In the same furnace, TiO_2 -containing glasses were melted in air. The glass batches were melted at 1550 °C for approximately 2 h in a platinum crucible. The glass compositions and preparation conditions are summarized in Table 1. The glass melts were homogenized by stirring with a platinum stirrer during melting, following which they were poured onto a carbon plate to form slab samples. These samples were annealed at 800 °C for 30 min in another furnace, followed by slow cooling (i.e., 1 °C/min) to room temperature.

2.2. Crystallization process

The glass transition temperature T_g and crystallization temperature T_c of the glasses were measured by differential thermal analysis (DTA) with a Bruker TG-DTA 200SA at a heating rate of 10 °C/min. Using glass powders with particle sizes of 212–415 μm . Considering the glass transition temperature and crystallization temperature of the glasses, they were crystallized using the heat treatment depicted in Fig. 2.

To acquire detailed data on the early stage of crystallization, the heat treatment of some samples was stopped at 1000 or 1100 °C. These glass-ceramic samples were cut and polished as required for characterization.

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