Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Non-Crystalline Solids 351 (2005) 2133–2137
JOURNAL OF NON-CRYSTALLINE SOLIDS
www.elsevier.com/locate/jnoncrysol

Nucleation and crystallization behavior of Li_2O–Al_2O_3–SiO_2 system glass–ceramic containing little fluorine and no-fluorine

Xingzhong Guo *, Hui Yang, Ming Cao

Center of Nano-Science and Nano-Technology of Zhejiang, Department of Materials Science and Engineering, Zhejiang University, Xihu District, Hangzhou 310027, China

Received 28 September 2004
Available online 20 June 2005

Abstract

The nucleation and crystallization behavior of Li_2O–Al_2O_3–SiO_2 system (LAS) glass–ceramics containing little fluorine and no-fluorine are investigated by the differential thermal analysis (DTA), X-ray diffraction (XRD), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). TEM of the annealed glass shows that the nucleation has appeared during the annealing stage. DTA of pre-nucleated glass shows that the optimum nucleating temperature of the LAS glass containing fluorine is 620 °C and 40 °C lower than that containing no-fluorine. XRD and SEM show that the optimum crystallizing temperature of the LAS glass containing fluorine is 760 °C, 110 °C lower than that containing no-fluorine, and the optimum crystallizing time is 4 h. The introduction of fluorine can decrease the crystallizing peak temperature (T_p) and the crystallizing activation energy (E) and improve the crystallization stage to obtain fine crystal with a size of 150 nm.

1. Introduction

Glass–ceramics, prepared by the controlled crystallization of glasses, possess uniform reproducible fine grain microstructures without porosity, and with its wide ranging outstanding properties, glass–ceramic has been used in spaceflight, chemistry, nucleation, mechanism, electron and magnetism fields [1]. The ternary (Li_2O–Al_2O_3–SiO_2, LAS) system glass–ceramic with low-expansion, highly thermal shock resistant and chemical durable is known as transparent and opaque cooking ware, cooker range tops, heat-resistant windows and telescope mirror blanks [2,3]. Since the nucleation stage is very important in controlling the crystallization stage to obtain a fine microstructure, the present studies on the nucleation stage of glass–ceramic are concentrated on the nucleation phase and its effects on the properties and structure of glass–ceramic. Riello [4] studied the nucleation behavior of LAS glass–ceramic to obtain the nucleation phase and its concentration. Bengisu [5] studied the long-term heating and thermal cycling of LAS glass–ceramic and found that the sample by nucleation at a lower temperature has more advantages than that at a higher one. In this paper, the DTA, XRD, TEM and SEM are employed to establish the optimum temperature and time for the nucleation and crystallization of the glass–ceramic and the effects of F^- ion on the nucleation and crystallization are also studied.

2. Experimental

2.1. Starting materials and glass preparation

The compositions (wt%) of the glass are: Li_2O (3.5), Al_2O_3 (19.8), SiO_2 (67.5), TiO_2 (4.2), Na_2O (2.5), MgO (2.5), K_2O (0.5) and F^- (0.8) (or no F^-). TiO_2 and

* Corresponding author. Tel.: +86 571 87951408; fax: +86 571 87953054.
E-mail address: gxzh_zju@163.com (X. Guo).

0022-3093/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jnoncrysol.2005.04.071

MgO are introduced as nucleation agent, Na_2O and K_2O are used to reduce the melting temperature and viscosity of the glass and improve the glass workability, while F^- is used as nucleation accelerant agent. The glass raw materials are melted at 1550–1600 °C and moulded in a pre-heated die. The glass is annealed at 580–620 °C for some time to eliminate internal stress. The glass samples are prepared for the heat-treatment.

2.2. Heat treatment and characterization of glass–ceramic

2.2.1. Nucleation stage

The glass samples are pre-nucleated at 560–660 °C (every 20 °C) for 2 h with a heating rate of 20 °C/min. Subsequently, the pre-nucleated samples are fast-cooled, ground and sieved through a 200-mech screen to obtain the glass powder. A differential thermal analyzer (NETZSCH STA 409 PC Luxx, Germany) with a heating rate of 20 °C/min is used to study the differential thermal analysis (DTA) of the glass powder. According to the crystallizing peak temperatures (T_p, temperature at exothermic peak of DTA curve) at different pre-nucleating temperatures, the optimum nucleating temperature can be obtained and the micrographics of the glass after annealed and nucleated at optimum nucleating temperature are carried out by transmission electron microscopy (TEM, model: Jeol JEM-200CX) and scanning electron microscopy (SEM, Model: FEI SIRION). The surface of the samples is finished and eroded by HF (2 wt%) for 30 s.

2.2.2. Crystallization stage

The heat-treatment of the annealed glass samples are carried out at 650–1150 °C with the heating rate of 20 °C/min. The samples are fast-cooled, ground and sieved through a 200-mech screen. Phase identification of the samples is performed by the X-ray diffraction (XRD) method on a XJ10-60 X-ray diffractometer using nickel filtered *CuKa* radiation in the range of $2\theta = 10$–$80°$ with a scanning speed of 2° per min, in order to obtain a optimum crystallizing temperature. With the nucleation at optimum nucleating temperature for 1 h, the crystallization of the samples are carried out at optimum temperature for 1 h, 4 h, 8 h, 12 h, respectively, and the SEM measurement is used to observe the grain size and crystal growth to obtain the optimum crystallizing time.

2.2.3. F^- ion effects on the heat treatment

The classic method, namely, grain growth activation energy method, is used to study the effect of F^- ion on the heat treatment. In this method, the different crystallizing peak temperatures (T_p) at different heating rates can be obtained to calculate the activation energy of crystallization. The effect of F^- ion is analyzed by crystallizing peak temperatures, crystallizing activation energy and glass structure.

3. Results

3.1. Investigation of the nucleation stage by DTA and TEM

Just as McMillan [6] said, the nucleation stage is difficult, but very important in the heat treatment system of glass ceramic. Many researchers have studied the nucleation of the glass by different methods. In those methods, the DTA analysis is considered as a relatively exact method to obtain the nucleating temperature. Due to many nuclei with a nanometer size forming in the pre-nucleating, the glass will absorb much thermal energy during continuous heat treatment or crystallization stage and the peak of crystallization is delayed in DTA curve. Here, we will utilize the theory to study the nucleation of the glass.

Fig. 1 shows the relationship between the crystallizing peak temperatures (T_p) and pre-nucleating temperatures. The lower crystallizing peak temperature indicates the higher crystallization rate, in order to obtain the optimum nucleating temperature. In Fig. 1, the T_p of the sample containing fluorine is 40–60 °C lower than those containing no-fluorine. According to the *a*-curve (containing fluorine), the lower T_p takes place at 620 °C and 660 °C, respectively. The lower T_p at 660 °C results from the energy change of grain growth at this pre-nucleating temperature, namely, the pre-nucleating temperature does not belong to the temperature range of the nucleation stage. Except for the T_p at 660 °C, the T_p at 620 °C is the lowest among the others, which indicates that the optimum nucleating temperature of the sample containing fluorine is 620 °C. With the same method, the optimum nucleating temperature

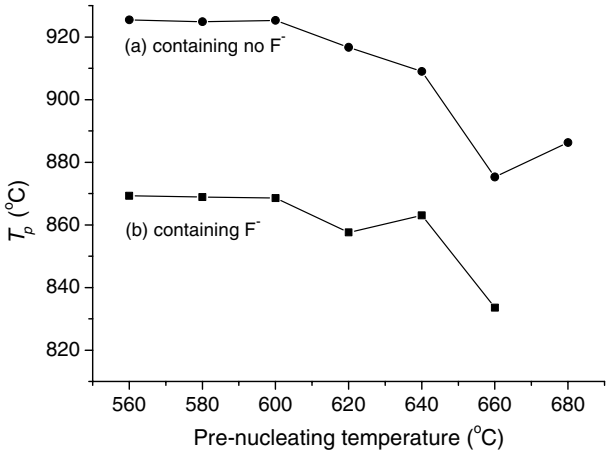

Fig. 1. Relationship between crystallization peak temperatures and pre-nucleating temperatures.