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Orientated crystallization of fresnoite glass-ceramics by using a thermal gradient

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Abstract

The glass with chemical composition (mol%) 33.33 BaO, 16.66 TiO_2, 50.00 SiO_2 was prepared by a conventional melt-quenching method. The glass-ceramics with a $Ba_2TiSi_2O_8$ crystal was prepared by crystallization of the glasses using a hot stage. The crystals are shown highly orientated along the *c*-axis perpendicular to the hot surface of the sample. Crystallization was controlled by a diffusion process with surface nucleation. The activation energy for crystallization was about 518 kJ/mol. The mechanism of oriented crystallization was considered in the present paper.
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Keywords: Fresnoite; Surfaces; Optical microscopy; Glass; Glass ceramics

1. Introduction

Fresnoite, $Ba_2TiSi_2O_8$, a mineral found in the sanbornite deposits of eastern Fresno County, California, USA, was first described by Alfors et al. in 1965.[1] Furthermore, the crystal structure was obviously shown by Moore in 1967.[2] Fresnoite is a tetragonal crystal in space group *P4bm*.

Recently, this material has received much attention for its pyroelectric, piezoelectric and surface acoustic wave properties.[3,4] Since the possibility of making a polar glass-ceramics by the crystallization of a glass has been demonstrated successfully, many additional investigations have been done because of some fabrication advantages.

Generally, the orientation growth of crystal may improve the physical properties.[5] From the previous study, an oriented glass-ceramics containing fresnoite prepared by electrochemical nucleation of a $BaO–TiO_2–SiO_2–B_2O_3$ melt had been presented.[6] In addition, induced polar orientation of $Ba_2TiSi_2O_8$ surface crystallized on glass due to ultrasonic surface treatment was reported.[7] However, such fabrication methods require a complicated apparatus, handling and an electric energy.

On the other hands, it was reported in the $Li_2Si_2O_5$ preparation that the degree of oriented crystallites in the isothermally crystallized glass-ceramics was poor compared to the samples crystallized in a temperature gradient.[8] However, this crystallization mechanism in orientation is not shown precisely.

This paper will present a consideration of the mechanism of oriented crystallization.

2. Experimental

The glass with chemical composition (mol%) 33.33 BaO, 16.66 TiO_2, 50.00 SiO_2 was prepared by using a conventional melt-quenching method. The raw materials of reagent grade oxides and carbonate, $BaCO_3$, TiO_2 and SiO_2, were mixed in the agate-mortar and melted at 1500 °C for 3 h in a platinum crucible. All chemicals were supplied by Kojundo Chemical Lab. Co., Ltd. The glass was obtained by pouring the melt on an iron plate. In order to remove a distortion of the glass, it was annealed at 650 °C for 12 h, and then cooled slowly to room temperature. This is the parent glass used in this study.

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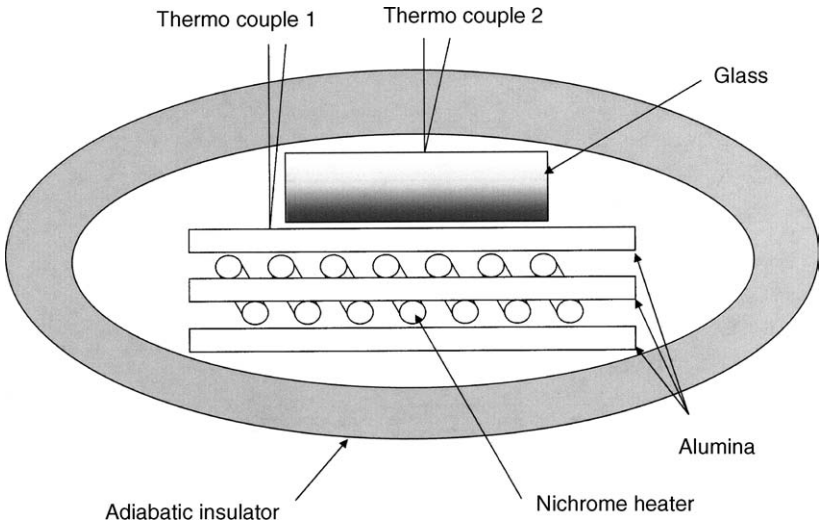

Fig. 1. Cross sectional view of the hot stage.

The hot stage shown in Fig. 1 was used to obtain the orientated glass-ceramics. The crystallization temperature is controlled by using a thermo couple 1, and the temperature gradient is indicated by using a thermo couple 2. The apparatus is available at the temperature up to 1100 °C. For the consideration of the crystallization mechanism from the glass, the crystallization was carried out in a temperature gradient below 60 °C by placing the polished glass on the hot stage of 810 and 850 °C, respectively. Various glass-ceramics prepared in the present study were ruptured for OM observations of the fine structure of crystallites near the surface.

The X-ray diffraction (XRD) profiles for the glass and the glass-ceramics were recorded using Cu Kα radiation with an X'pert Powder Diffract-meter System from Philips Co. Ltd. A scanning electronic microscope (SEM) photograph was collected by S-4700 of Hitachi High-Technologies Corporation, and the optical microscope (OM) photographs were obtained by ME600L from Nikon Corporation.

3. Results and discussion

The XRD profile of the sample crystallized in a uniform temperature is shown in Fig. 2a. The profile agrees with card data #89-0924 in JCPDS files, and the sample is assigned to the fresnoite. However, the XRD profiles of the samples crystallized on the hot stage shows predominantly (0 0 *n*) of the fresnoite phase, shown in Fig. 2b. That is, the glass-ceramics prepared with the temperature gradient shows the *c*-axis preferred orientation in the direction of normal to the surface. From a SEM photograph on the rupture surface of the glass-ceramics shown in Fig. 3, the crystallites of the microstructure near the surface are shown in a one-dimensional growth perpendicular to the surface. The crystallite outlines are observed in the rectangular shape vertically from the surface. That is, it was shown that the glass was crystallized in one-dimension

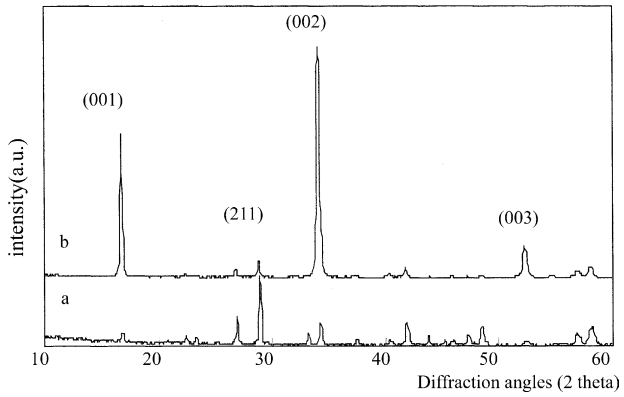

Fig. 2. XRD profiles of fresnoite glass-ceramics: (a) sample without temperature gradient; (b) sample with temperature gradient.

with *c*-axis preferred orientation under the temperature gradient.

The OM photographs of the crystal film prepared at various crystallizing times are shown in Fig. 4. The nucleation

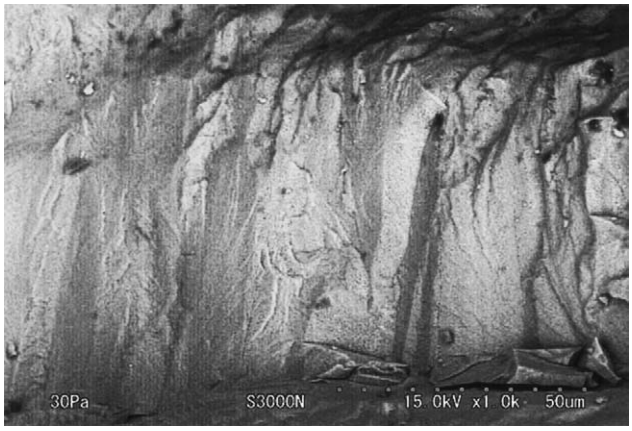

Fig. 3. SEM photograph of surface microstructure cross section.

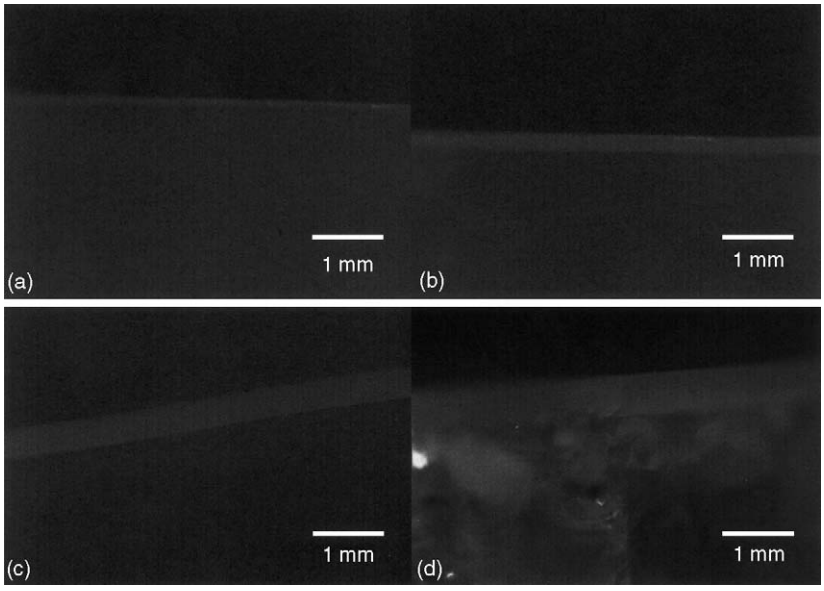

Fig. 4. OM photographs of cross section of the samples crystallized at 850 °C. Crystallization time: (a) 0.5 h; (b) 1.0 h; (c) 1.5 h; (d) 2.0 h.

occurred on the glass surface at the side of a hot stage after attained to the crystallization temperature. Crystallites grew by a uniform rate under the temperature gradient from surface to bulk after the surface was completely covered with the nuclear. The relation between the crystal thickness and the crystallization time at the 810 and 850 °C of crystallizing temperatures, respectively, is shown in Fig. 5. The crystal film grows linear with time as processes for diffusion-controlled growth.[9] The equation is expressed as:

$$u = va_0 \left[1 - \exp\left(\frac{-\Delta G}{kT}\right)\right] \quad (1)$$

where u is the growth rate per unit area of the interface, v is the frequency factor for transport at the crystal-glass interface, a_0 is the distance advanced by the interface in a unit kinetic process, approximately a molecular diameter, ΔG is the free-energy change accompanying crystallization, k is the Bolzman constant and T is the absolute temperature.

For evaluating ΔG by using u and T, the Eq. (1) is changed to the next Eq. (2):

$$\ln u = \frac{-\Delta G}{kT} + C \quad (2)$$

From the experimental results, the plot of $\ln u$ versus $1/T$ with the slope of $-\Delta G/k$ was given in Fig. 6 and ΔG was calculated to 518 kJ/mol. Therefore, the crystallization mechanism is surface nucleation and one-dimensional growth is controlled by diffusion.

In this study, an orientation index (OI) of fresnoite is defined as below:

$$\mathrm{OI} = \frac{(\mathrm{I}_{002} - 0.2\mathrm{I}_{211})}{(\mathrm{I}_{002} + 0.2\mathrm{I}_{211})} \quad (3)$$

where I_{002} is the XRD peak intensity of (0 0 2) reflection of fresnoite, and I_{211} is that of (2 1 1) reflection. With the increase in the temperature gradient, the orientation index grows large, which is also shown in the XRD profiles of Fig. 7.

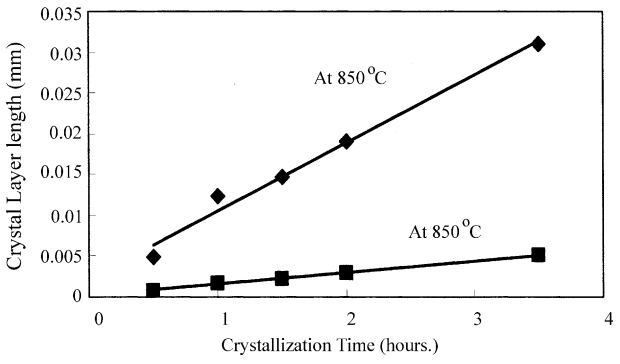

Fig. 5. Growth of crystals as affected by time and temperature.

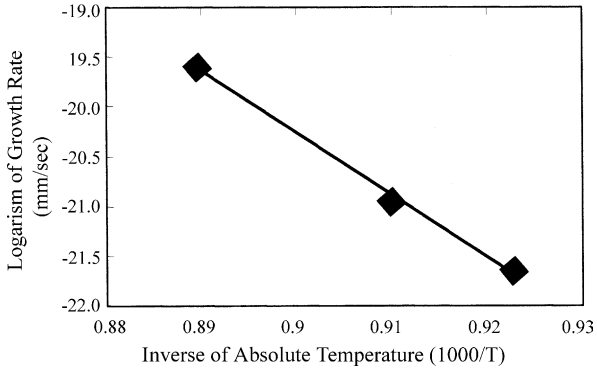

Fig. 6. Variation of growth rate with temperature.

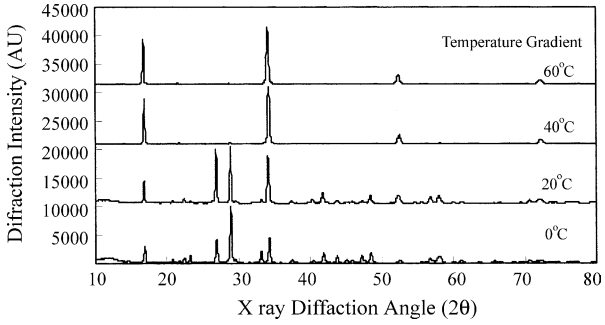

Fig. 7. XRD profiles of surface crystals with temperature gradient.

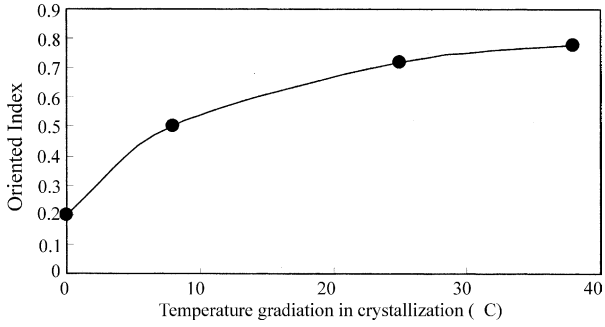

Fig. 8. Relation of orientation index with temperature gradient.

The relation between orientation index and temperature gradient is shown in Fig. 8.

From the above results, the diffusion controls the growth of crystallites. By the considerations of the thermodynamics, the temperature gradient can cause oriented diffusion. Therefore, the oriented growth depends on the temperature gradient. In summary, the temperature gradient is the most important to provide the driving force for the oriented growth in the glass.

Therefore, the crystallizing mechanism of the glass-ceramics prepared in the present study suggests that the surface nucleation occurred on the hot surface in contact with the hot stage, and the surface was completely covered with the nuclear, and the crystallites slowly crystallized from the surface along the temperature gradient and the preferred orientation crystallites in one-dimensional growth.

4. Conclusion

The crystallization of the glass with chemical composition (mol%) 33.33 BaO, 16.66 TiO_2, 50.00 SiO_2 is controlled by the diffusion process with surface nucleation. The glass-ceramics with oriented crystallites of $Ba_2TiSi_2O_8$ along with the *c*-axis perpendicular to the surface are prepared by using a hot stage. The degree of oriented growth depends on the temperature gradient. The activation energy for crystallization is about 518 kJ/mol.

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