JOURNAL OF MATERIALS SCIENCE 31 (1996) 4249–4253

Nucleation and crystallization kinetics of $CaO–Al_2O_3–2SiO_2$ in powdered anorthite glass

H. C. PARK, S. H. LEE, B. K. RYU
Department of Inorganic Materials Engineering, Pusan National University, Pusan 609-735, Korea
M. M. SON, H. S. LEE
Department of Ceramics, Daegu Technical College, Daegu 704-120, Korea
I. YASUI
Institute of Industrial Science, The University of Tokyo, Tokyo 106, Japan

The nucleation and crystallization kinetics of $CaO–Al_2O_3–2SiO_2$ crystals in powdered anorthite glass with particle size <44 μm in which $CaO–Al_2O_3–2SiO_2$ crystals were found to crystallize in the heating process of the glass, were studied by nonisothermal measurements using differential thermal analysis (DTA). The temperature of maximum nucleation rate was determined from the DTA curves of samples heat treated at different temperatures. The activation energy and kinetic parameters were simultaneously calculated from the DTA data using previously reported kinetic models. The crystallization process of a sample heat treated at the temperature of the maximum nucleation rate was fitted to kinetic equations with an Avrami constant, $n \cong 2$ and a dimensionality of crystal growth, $m \cong 2$, indicating that the constant number of nuclei of $CaO–Al_2O_3–2SiO_2$ precipitated in a glass matrix grew two-dimensionally with an activation energy taken as an average of the values calculated by the Kissinger and also the Augis and Bennett method of 679 ± 4 kJ mol^{-1}.

1. Introduction

Glass–ceramics, prepared by the controlled devitrification of glasses, have become established in a wide range of technical and technological applications [1]. One of these recent applications is as substrate materials for semiconductor packaging [1–4].

A relatively new method of glass–ceramic preparation is the sintering of glass powders, followed by a nucleation heat treatment [5–7]. We have recently examined the possibility of using a glass powder with the composition of anorthite ($CaO–Al_2O_3–2SiO_2$) in order to prepare glass–ceramic substrates using a low sintering temperature [8]. It was found that the glass powder sintered above 900 °C and that an anorthite phase was obtainable in the glass. The formation process of such anorthite crystals is of great importance both from a technological aspect as well as a fundamental point of view. In order to clarify the formation process of such materials, it is essential to study the temperature range where nucleation can occur, the temperature where the nucleation rate is a maximum, and the crystallization kinetics.

A number of studies have been reported that also examined the sintering and crystallization mechanisms of cordierite-based glasses [9–16], and determined the kinetic parameters [17–19]. However, to our knowledge, there has been no systematic study on the nucleation and the crystallization kinetics of anorthite glass with only some preliminary data reported by Ota *et al.* [20] currently available in the literature.

In the present work, we focus our attention on the nucleation and crystallization kinetics in powdered anorthite glass, in which $CaO–Al_2O_3–2SiO_2$ crystals precipitated during the heating process of the glass. We performed nonisothermal measurements using differential thermal analysis (DTA) for the study.

2. Experimental procedure

2.1. Glass preparation

Glass with the composition $CaO–Al_2O_3–2SiO_2$ (mol ratio) was used. The glass was prepared by melting a homogeneous mixture of reagent-grade $CaCO_3$, Al_2O_3, and SiO_2 at 1600 °C for 2 h in a Pt–Rh crucible. The melt was quenched by pouring it into water. The as-quenched glass was ground and screened with a size of 44 μm mesh, and stored in an oven at 100 °C to prevent moisture attack until it was required for the nonisothermal DTA measurements using a Macscience model TG-DTA 2000.

2.2. Methods of analysis

In order to determine the temperature range for nucleation, T_n and the maximum nucleation rate temperature, T_{mn}, heat treatments and DTA experiments were performed, respectively. The heat treatments

0022–2461 © *1996 Chapman & Hall*

were performed as follows; 50 mg of the sample with a particle size of < 44 μm were placed in an alumina boat and heated up to appropriate temperatures at a rate of 10 °C per min in an electrical resistance furnace. The sample was taken out of the furnace after a holding period of 2 h at the temperature, T_n and was allowed to cool in an ambient atmosphere. The DTA measurements were performed using about 30 mg of the heat-treated glass powder (< 44 μm) in a Pt crucible in an air atmosphere with a heating rate of 10 °C per min.

In order to determine the kinetic parameters of the sample heat treated at the previously determined T_{mn}, DTA measurements were also performed using about 30 mg of the heat-treated glass powders in an air atmosphere with heating rates of 5, 10, 15, and 20 °C per min, respectively to 1050 °C. The DTA results were further analysed to obtain the crystallization mode and the activation energy values for crystallization of each sample using the Kissinger [21], Ozawa [22], and Augis–Bennett [23] methods. The reason that all of these methods were used in the present study was to obtain more accurate kinetic parameters for the glass. The phase analysis and crystallization of the heat-treated samples were examined by X-ray diffraction (XRD: Rigaku RINT 2000, Japan) and scanning electron microscopy (SEM: Jeol JSM-5400, Japan). A best fit for the results was calculated by the least square method. The arithmetic mean as well as the standard deviation were calculated for the activation energies.

3. Results and discussion

3.1. Nucleation and temperature of maximum nucleation rate

As reported by Marotta *et al.* [24] and Xu *et al.* [25], the DTA technique can be used to determine the nucleation temperature range and the temperature for maximum nucleation. In the DTA technique, the temperature at the crystallization peak maximum, T_p is determined as a function of the nucleation temperature, T_n, using a constant sample weight and heating rate. The inverse of the temperature corresponding to the maximum of the DTA crystallization peak, $1/T_p$, obtained for this glass nucleated at different T_n for 2 h, is shown in Fig. 1. For samples with the same composition, the following relationship [25, 26] is applied between the number of nuclei, N and the crystallization peak temperature, T_p when the heating rates are the same for the DTA runs.

$$\ln N = \frac{E_c}{R}\frac{1}{T_p} + \text{constant} \qquad (1)$$

Thus, the greater the number of nuclei, the lower the crystallization temperature. Therefore, the change in T_p in Fig. 1 with T_n is primarily due to a change in N in the glass.

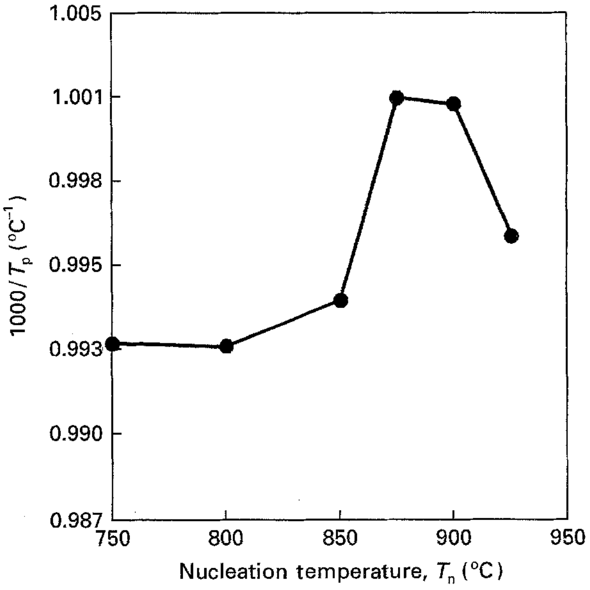

Figure 1 Inverse of T_p for the anorthite glass as function of T_n. Particle size and weight of each sample were held constant at < 44 μm and 50 mg, respectively. Each sample was held at T_n for 2 h and $\phi = 10$ °C per min.

As shown in Fig. 1, $1/T_p$ is constant until the glass is nucleated above 850 °C, indicating that the nucleation rate for this glass below 850 °C is so low that no detectable number of new nuclei are formed in 2 h as compared with the number of nuclei initially present in the as-quenched glass. Fig. 1 further shows that the temperature where the nucleation can occur in the anorthite glass ranges from 850–910 °C and that the nucleation rate is a maximum at 880 ± 5 °C. The crystallization peak on the DTA curves for the glass heat treated at temperatures higher than 910 °C became weak and finally disappeared.

To confirm the nucleation results on the DTA curves, XRD analysis was performed. The XRD patterns of the as-quenched glass and the glass heat treated at 880 °C (the temperature of the maximum nucleation rate) for 2 h have broad humps characteristic of the amorphous state, whereas the glasses heat treated at a temperature higher than 950 °C for 2 h show diffraction peaks belonging to crystalline anorthite, $CaO–Al_2O_3–2SiO_2$ as is shown in Fig. 2.

3.2. Kinetic parameters of crystal growth

The DTA data were analysed primarily using the Kissinger equation:

$$\ln\left(\frac{\phi}{T_p^2}\right) = -E_{ck}/RT_p + \text{constant} \qquad (2)$$

where ϕ is the DTA heating rate, T_p is the crystallization peak temperature, E_{ck} is the activation energy for crystallization estimated by the Kissinger method, and R is the gas constant.

The Kissinger plot according to Equation 2 for the glass, for heating rates of 5, 10, 15, and 20 °C per min, is shown in Fig. 3. The value of E_{ck} determined from the slope of this plot is 683 kJ mol^{-1}. Matusita and Sakka [27] have stated that Equation 2 is valid only if crystal growth occurs on a fixed number of nuclei. A sample of the investigated glass was nucleated at the temperature of the maximum nucleation rate and the number of nuclei formed during the DTA run can be regarded as negligible [24]. Therefore, Equation 2 is applicable for the study.

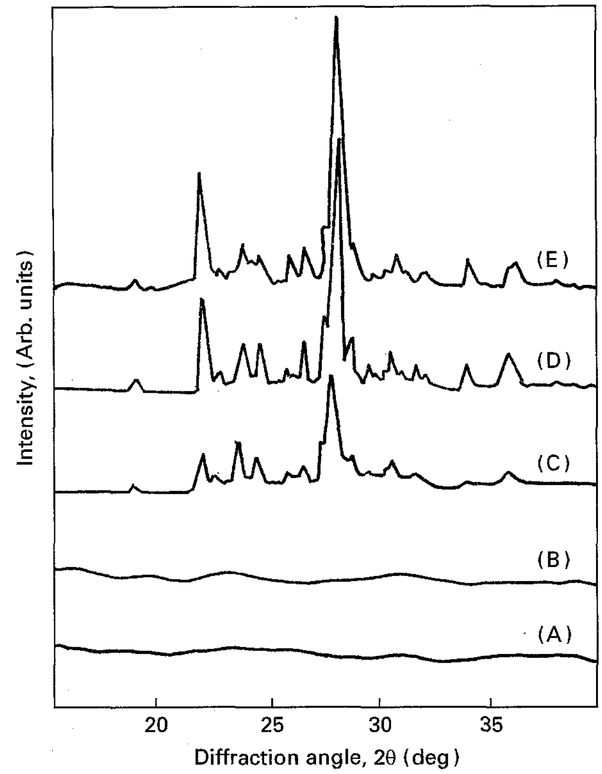

Figure 2 XRD patterns of the anorthite glass powder: (A) as-quenched; (B) nucleated at 880 °C for 2 h; and (C)–(E) nucleated at temperatures of 950 °C, 1000 °C, and 1050 °C for 2 h, respectively.

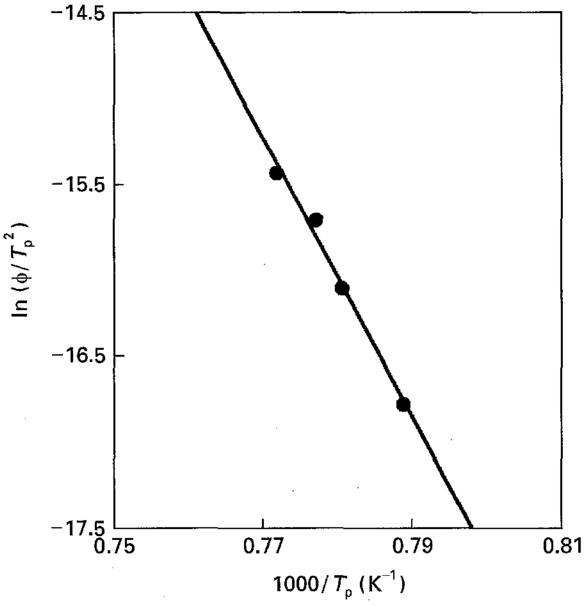

Figure 3 Kissinger plot for the anorthite glass powder for ϕ of 5, 10, 15, and 20 °C per min. The sample was nucleated at 880 °C for 2 h.

TABLE I Values of n and m for different crystallization mechanisms in the heating process

Crystallization mechanism	n	m
Bulk crystallization with a constant number of nuclei (i.e. the number of nuclei is independent of the heating rate)		
three-dimensional growth of crystals	3	3
two-dimensional growth of crystals	2	2
one-dimensional growth of crystals	1	1
Bulk crystallization with an increasing number of nuclei (i.e. the number of nuclei is inversely proportional to the heating rate)		
three-dimensional growth of crystals	4	3
two-dimensional growth of crystals	3	2
one-dimensional growth of crystals	2	1
Surface crystallization	1	1

If most nuclei are formed during the DTA run, then the activation energy values from the Kissinger equation are incorrect. Matusita and Sakka have suggested a modified form of the Kissinger equation of

$$\ln(\phi^n/T_P^2) = -mE_c/RT_P + \text{constant} \qquad (3)$$

where E_c indicates the correct activation energy for crystallization via the modified Kissinger method, n is an Avrami constant, and m is the dimensionality of the crystal growth. The parameters n and m that are characteristic of various crystallization mechanisms can take on various values [19, 28, 29], as is summarized in Table I. The value of m is related to n as: $m = n$ when crystallization at different heating rates occurs on a fixed number of nuclei. In other words the number of nuclei is constant during the DTA runs at different values for ϕ. In addition, when surface nucleation dominates, $m = n = 1$ and Equation 3 essentially reduces to the Kissinger Equation 2.

Xu *et al.* [25] have demonstrated that for most oxide-glass systems that E_c and E_{ck} are related by the equation:

$$E_c \cong (n/m)\,E_{ck} \qquad (4)$$

For $m = n$, i.e., when crystallization occurs on a fixed number of nuclei, $E_{ck} = E_c$. Thus, for crystal growth that occurs on a fixed number of nuclei, the analysis of DTA data by the Kissinger model, Equation 2 yields the correct value of E_c. The parameters, n and m in this study are hence considered to be $n = m$, as is obvious from Table I.

The value of n can be determined by the Ozawa equation [22, 25]:

$$\left[\frac{d\ln(-\ln(1-x))}{d\ln\phi}\right]_T = -n \qquad (5)$$

where x is the volume fraction crystallized at a fixed temperature T when heated at ϕ. This is, x is the ratio of the partial area at T to the total area of the crystallization exotherm. An Ozawa plot from Equation 5 is presented in Fig. 4, and indicates that bulk crystallization dominates in the glass ($n = 1.9$). Thus, the m value of the glass becomes ~ 2 because n equals m, that is $n = m$ as mentioned previously. Allowing for experimental errors, the value of n is considered to be 2. On the basis of the SEM observation for the cross-section of the glass which was heated up to 1000 °C, held for 2 h, and furnace cooled, where the crystallization was almost completed, particles of CaO–Al_2O_3–$2SiO_2$ grown in two dimensions are observed in the glass matrix, indicating $m = 2$, as shown in Fig. 5.

To further confirm the accuracy of the above result for activation energy value, the following Augis and

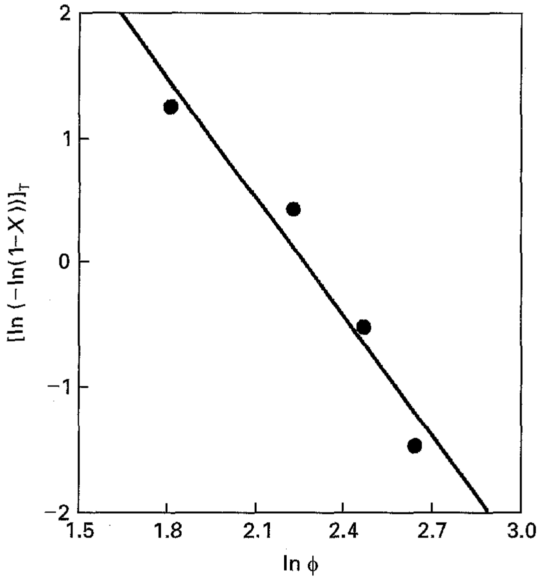

Figure 4 Plot of $[\ln(-\ln(1-x))]_T$ versus $\ln \phi$ for the anorthite glass powder for a ϕ of 5, 10, 15 and 20 °C per min. The sample was nucleated at 880 °C for 2 h.

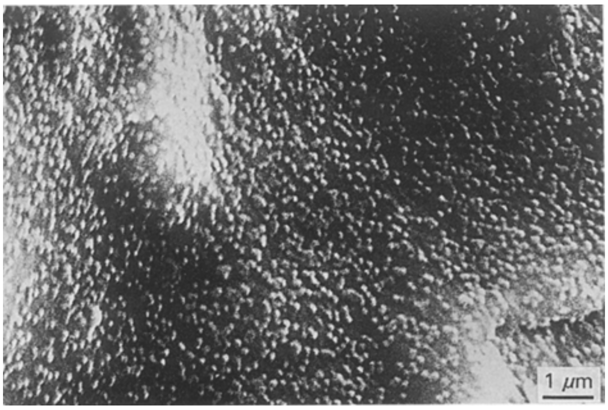

Figure 5 SEM micrograph of the anorthite glass heat treated at 1000 °C for 2 h ($\phi = 10$ °C per min), furnace cooled, and etched at 25 °C with 1% HF for 20 sec. Prior to the heat-treatment, the sample was nucleated at 880 °C for 2 h and a $\phi = 10$ °C per min.

Bennett [23] equation can be applied:

$$\ln(\phi/(T_P - T_0)) = -E_{cab}/RT_P + \text{constant} \quad (6)$$

where T_0 is the initial temperature from which the sample was heated with a constant heating rate which is 300 K for the present study. E_{cab}, which indicates the activation energy for crystallization from the Augis and Bennett method, can be calculated from the plot of $\ln(\phi/(T_P - T_0))$ versus $1/T_P$, as is shown in Fig. 6.

The activation energy value of 675 kJ mol^{-1} from this method is in good agreement with that of 683 kJ mol^{-1} Kissinger method. Thus an averaged value of the activation average can be taken to be 679 ± 4 kJ mol^{-1}.

4. Conclusions

From the experimental results the following conclusions can be drawn:

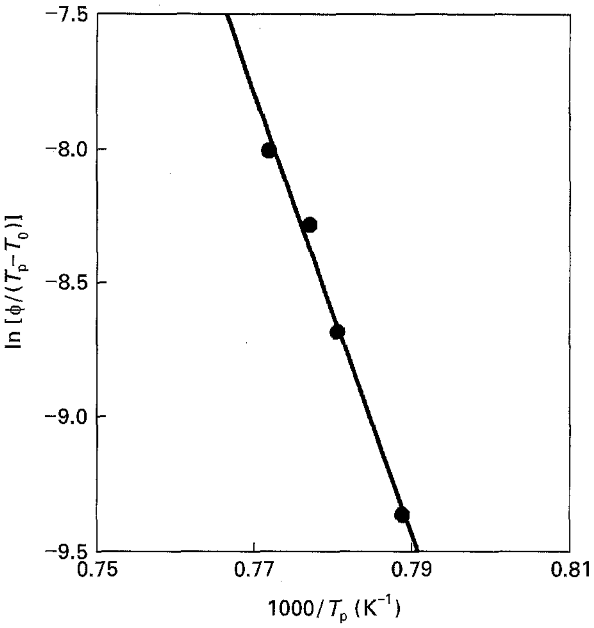

Figure 6 Plot of $\ln(\phi/(T_P - T_0))$ versus $1000/T_p$ for the anorthite glass for ϕ of 5, 10, 15, and 20 °C per min. The sample was nucleated at 880 °C for 2 h.

1. The temperature of maximum nucleation rate for $CaO–Al_2O_3–2SiO_2$ crystals in the powdered anorthite glass (grainsize < 44 µm) is around 880 °C.
2. The values of n and m depend on the crystal growth mechanism and are found to be $n = m \cong 2$ from the nonisothermal DTA measurements. The crystallization mechanism for the powdered glass is two-dimensional growth.
3. The activation energy of crystal growth, E_c, for the powdered anorthite glass obtained from the average of the values calculated using the nonisothermal kinetic equations is 679 ± 4 kJ mol^{-1}.

Acknowledgements

Financial support for the present work was provided by the Korean Ministry of Education and Pusan National University. This support is gratefully acknowledged.

References

1. G. PARTRIDGE, *Glass Technology* **35** (1994) 116.
2. R. R. TUMMALA, *J. Amer. Ceram. Soc.* **74** (1991) 895.
3. S. H. KNICKERBOCKER, A. H. KUMAR and L. W. HERRON, *Bull. Amer. Ceram. Soc.* **72** (1993) 90.
4. Y. SUNG, S. A. DUNN and J. A. KOUTSKY, *J. Euro. Ceram.* **14** (1994) 455.
5. E. M. RABINOVICH, *J. Mater. Sci.* **20** (1985) 4259.
6. E. A. GIESS, J. P. FLETCHER and L. W. HERRON, *J. Amer. Ceram. Soc.* **67** (1984) 549.
7. S. KNICKERBOCKER, M. R. TUZZOLO and S. LAWHORNE, *ibid.* **72** (1989) 1873.
8. B. RYU and I. YASUI, *J. Mater. Sci.* **29** (1994) 3323.
9. R. MORRELL, *Proc. Brit. Ceram. Soc.* **28** (1979) 53.
10. Y. HIROSE, H. DOI and O. KAMIGAITO, *J. Mater. Sci. Lett.* **3** (1984) 153.
11. D. R. BRIDGE, D. HOLLAND and P. W. McMILLAN, *Glass Technology* **26** (1985) 286.
12. M. A. McCOY and A. H. HEUER, *J. Amer. Ceram. Soc.* **71** (1988) 673.

13. M. AWANO, H. TAKAS and Y. KUWAHARA, *ibid.* **35** (1992) 2535.
14. S. H. KNICKERBOCKER, A. H. KUMAR and L. W. HERRON, *Bull. Amer. Ceram. Soc.* **72** (1993) 90.
15. A. G. GREGORY and T. J. VEASEY, *J. Mater. Sci.* **6** (1971) 1312.
16. K. WATANABE, E. A. GIESS and M. W. SHAFER, *J. Mater. Sci.* **20** (1985) 508.
17. T. MULLER, *J. Therm. Anal.* **35** (1989) 823.
18. T. RUDOLPH, W. PANNHORST and G. PETZOW, *J. Non-Cryst. Solids* **155** (1993) 273.
19. I. W. DONALD, *J. Mater. Sci.* **30** (1995) 904.
20. R. OTA, H. KURIBAYASHI, J. FUKUNAGA and T. TAGUCHI, *J. Non-Cryst. Solids* **144** (1992) 81.
21. H. E. KISSINGER, *J. Res. Natl. Bur. Stand. (US)* **57** (1956) 217.
22. T. OZAWA, *Polymer* **12** (1971) 150.
23. J. A. AUGIS and J. E. BENNETT, *J. Therm. Anal.* **13** (1978) 283.
24. A. MAROTTA, A. BURI and F. BRANDA, *J. Mater. Sci.* **16** (1981) 341.
25. X. J. XU, C. S. RAY and D. E. DAY, *J. Amer. Ceram. Soc.* **74** (1991) 909.
26. L. ZHIEN, S. YIHUI, D. XIJIANG and C. JIJIAN, *J. Mater. Sci.* **30** (1995) 390.
27. K. MATUSITA and S. SAKKA, *J. Non-Cryst. Solids* **38–39** (1980) 741.
28. P. J. HAYWARD, E. R. VANCE and D. C. DOERN, *Bull. Amer. Ceram. Soc.* **66** (1987) 1620.
29. A. TANIGUCHI, M. TATSUMISAGO and T. MINAMI, *J. Amer. Ceram. Soc.* **72** (1995) 460.

Received 23 August 1995
and accepted 15 January 1996