

Crystallization kinetics for the synthesis of hyper-structures in P_2O_5 -ZnO- B_2O_3 - Al_2O_3 - TiO_2 glass ceramic composite

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The nucleation and crystallization kinetics of P_2O_5 - B_2O_3 -ZnO- Al_2O_3 - TiO_2 crystals in bulk glass in which these crystals were found to crystallize in the heating process of the glass, were studied by non-isothermal measurements using differential thermal analysis (DTA). A nucleation rate-temperature was determined by plotting either the reciprocal of the temperature corresponding to the crystallization peak maximum, $1/T_p$, or the height of the crystallization peak, $(\Delta T)_p$, as a function of nucleation temperature, T_n . The temperature where nucleation can occur for this glass ranges from 720 °C to 860 °C and the temperature for maximum nucleation is 820 ± 5 °C. The correct activation energy for crystallization, E_c , for this glass is the same for surface and/or bulk crystallization, and is 23 ± 15 kcal/mol. The analysis of the crystallization data with the Kissinger equation and the Marotta equation yields the correct value for E_c only crystal growth occurs on a fixed number of nuclei. 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, $n \approx 3$, 1 and a dimensionality of crystal growth, $m \approx 3$, 1.

Key words: Crystallization kinetics, Phosphate glass, Glass-ceramics, Surface nucleation.

Introduction

Glass-ceramics, prepared by the controlled devitrification of glasses, have become established in a wide range of technical and technological applications [1]. Parameters should be known for a glass: these applications include the temperature range where nucleation can occur. Also the temperature at which the nucleation rate is a maximum, the activation energy, and the dimensionality of crystal growth. The technique [2, 3] commonly used to determine the nucleation rate is to heat the glass at a certain temperature for a selected period of time, thereby developing some number of nuclei within the glass.

The differential thermal analysis (DTA) technique can also be used as an alternative method to determine the nucleation temperature range and the temperature for maximum nucleation. The advantage of the DTA technique is that it requires much less time than that needed for the classical technique and is more convenient for experimental data analysis. One of the recent applications is as low sintering temperature and functional melts materials with non-Pb containing glasses without harmful heavy metals. To our knowledge, there has been no systematic study on the nucleation and the crystallization kinetics of this glass with only some preliminary data.

In the present study, we focus our attention on the nucleation and crystallization kinetics in the glass, in

which P_2O_5 - B_2O_3 -ZnO- Al_2O_3 - TiO_2 crystals precipitated during the heating process of the glass.

Experimental Procedures

Glass preparation

Glass with a composition 55 P_2O_5 -15 B_2O_3 -35ZnO-3 Al_2O_3 -6 TiO_2 (wt%) was used. The glass was prepared by melting a homogeneous mixture of reagent-grade P_2O_5 , B_2O_3 , ZnO, Al_2O_3 and TiO_2 at 1300 °C for 1h in an alumina crucible. The melt was quenched by pouring on a plate. The as-quenched glass was ground and screened with a mesh size of 44 μ mesh, and stored in an oven at 100 °C to prevent problem with moisture.

Measurements

Glass powder with a weight of 30 mg was contained in a platinum crucible and the reference material was α - Al_2O_3 powder. The data were recorded by means of a chart recorder. The samples were heated in air from ambient temperature to 1000 °C at heating rates of 5, 10, 15 and 20 K/min.

The DTA results were further analyzed to obtain the crystallization mode and the activation energy values for crystallization of each sample using the Kissinger [4] and the Marotta and Buri[5] methods. The reason that these methods were used in the present study was to obtain more accurate kinetic parameters for the glass. The amount and types of crystalline phases existing in a sample after heat treatment were determined by XRD using Cu K α radiation, and a working voltage 25 kV. After crystallization, the samples were polished and etched

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in 1% hydrofluoric acid for 1 s (25), then washed, dried and coated with gold in an ion beam coater, and analyzed by SEM (HITACHI S3500N).

Result and Discussion

Nucleation and temperature of maximum nucleation rate

As reported by Marotta *et al.* [6] and Xu *et al.* [7], 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 maximum crystallization peak, T_p is determined as a function of the nucleation temperature, T_n , using a constant sample weight and heating rate. Typical DTA traces of the samples crystallized at heating rates of 5, 10, 15 and 20 K/min are shown in Fig. 1. The glass transition temperature (T_g) of all curves was evidently about 524 °C. The DTA curves exhibited three distinct exothermic peaks indicating the formation of three crystalline phases.

Table 1 shows the values of the crystallization peak temperature (T_p) of DTA experiments of samples at different heating rates. When the heating rate was 15 K/min, three exothermic peaks were exhibited at 700 °C, 822 °C and 852 °C. 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 1 h, is shown in Fig. 2. For samples with the same composition, the following relationship [7, 8] 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:

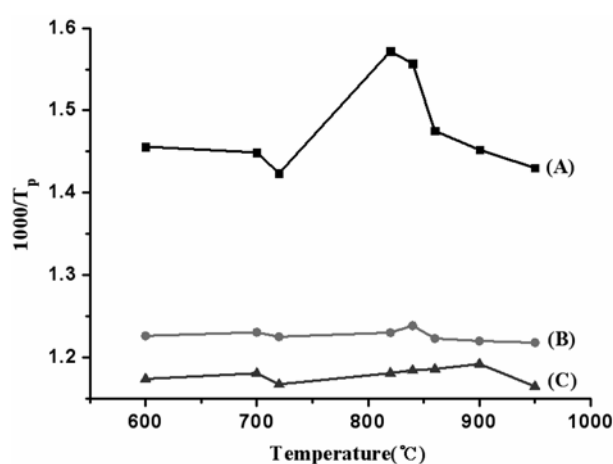


Fig. 2. Inverse of T_p for the P_2O_5 - B_2O_3 -ZnO-BaO- Al_2O_3 added TiO_2 glass function of particle size and weight of each sample were held constant at $< 44 \mu m$ and 30 mg, respectively. Each sample was held at T_n for 1 h and $\alpha = 15^\circ C/min$. (A) T_{p1} , (B) T_{p2} and (C) T_{p3} .

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

Larger numbers of nuclei have a lower crystallization temperature. Therefore, the change of T_p in Fig. 2 with T_n is primarily due to a change in N of the glass. As shown in Fig. 2, $1/T_{p1}$, $1/T_{p2}$ and $1/T_{p3}$ show where the nucleation rate is a maximum in the P_2O_5 - B_2O_3 -ZnO- Al_2O_3 - TiO_2 system glass at 820 °C, 840 °C and 900 °C, respectively.

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 600 °C and 700 °C for 1 h have humps characteristic of the amorphous state, whereas the glasses heat treated at a temperature higher than 720 °C for 1 h show diffraction peaks belonging to crystalline of α - $Ti_4P_2O_7$ and $AlPO_4$, is shown in Fig. 3. The glass heat treated at 720 °C was shown weak intensity of XRD peaks.

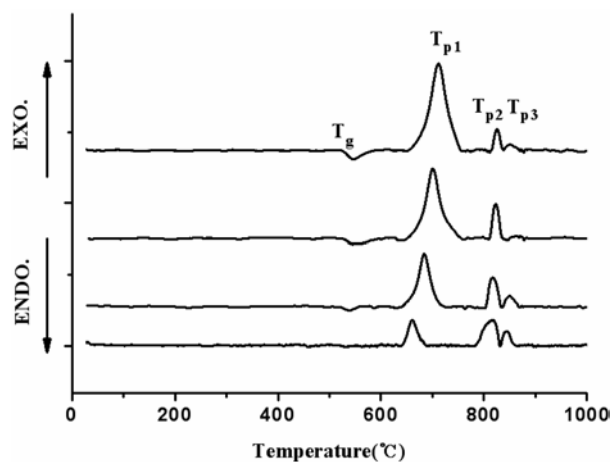


Fig. 1. DTA curves of the glass samples at heating rates of (A) 5 °C/min, (B) 10 °C/min, (C) 15 °C/min and (D) 20 °C/min.

Table 1. Values of T_p^* at different heating rates α of DTA

Heating rates (°C/min)	T_{p1}	T_{p2}	T_{p3}
5	661	814	842
10	684	816	850
15	700	822	852
20	711	825	851

* T_p : crystallization peak

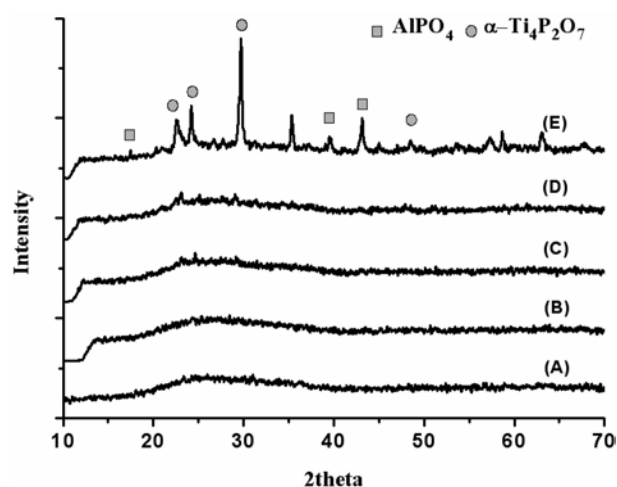


Fig. 3. XRD patterns of the P_2O_5 - B_2O_3 -ZnO- Al_2O_3 added TiO_2 glass (A) as-quenched, (B) nucleated at 600 °C for 1 h; (C)-(E) nucleated at temperatures of 700 °C (T_{p1}), 720 °C (T_{p2}), 820 °C (T_{p3}) for 1 h, respectively.

Kinetic parameters of crystal growth

The DTA data were analyzed primarily using the Kissinger [9] equation:

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

where, α 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 plots according to Equation (2) for the glasses, for heating rates of 5, 10, 15 and 20 K/min with T_{p2} samples are shown in Fig. 4. The values of E_c determined from the slope of these plots are given in Table 2. Matsusita and Sakka [10] have stated that Equation (2) is valid only if crystal growth occurs on a fixed number of nuclei. A sample of the maximum nucleation rate and the number of nuclei formed during the DTA run can be regarded as negligible [11]. Therefore, Equation (2) is applicable for the study. Matsusita and Sakka [10] have suggested a modified form of the Kissinger equation:

$$\ln\left(\frac{\alpha^n}{T_p^m}\right) = -\frac{mE_c}{RT_p} + \text{constant} \quad (3)$$

where, α is the DTA heating rate, T_p is the crystallization peak temperature, E_c is the activation energy for crystallization, and n is the value of the Avrami constant. The parameters n and m that are characteristic of various crystallization mechanisms can take on various values [12, 13, 14]. The value of m is related to n as: $m = n$

when crystallization at different heating rates occurs on a fixed number of nuclei. On the other hands, the number of nuclei is constant during the DTA runs at different values for α . In addition, when surface nucleation dominates, $m = n = 1$ and Equation. Xu *et al.* [7] have demonstrated that with 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 $n = m$ [15]. The value of n can be determined by the Marotta and Buri [5] equation:

$$\ln\alpha = -\frac{E}{RT_p} + \text{constant} \quad (4)$$

$$\ln\Delta T = -\frac{nE}{RT_p} + \text{constant}$$

where, α is the DTA heating rate, T_p is the crystallization peak temperature, E is the activation energy for crystallization. And ΔT is the deflection from the baseline of the curve. The Marotta plots according to Equation (4) for the glass, for heating rates of 5, 10, 15 and 20 °C/min with T_{p2} sample (Fig. 5), and indicates that bulk crystallization dominates in the glass, as is presented in Table 2. Thus, the m value of the glass becomes ≈ 3 because n equals m as mentioned previously. Allowing for experimental errors, the value of n is considered to be 3.

Microstructure

As discussed above, temperature and time for nucleation

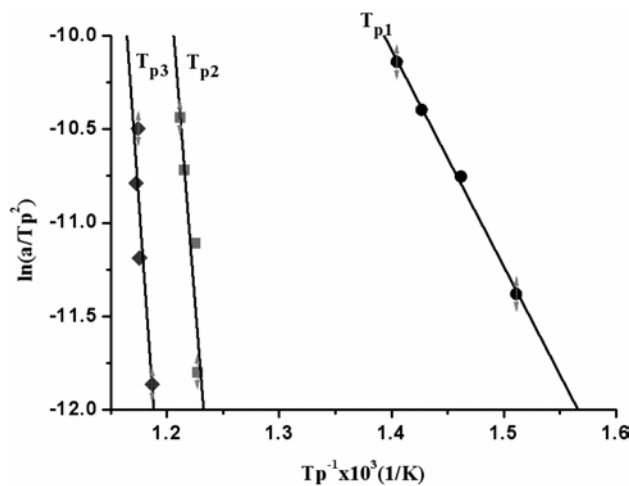


Fig. 4. Kissinger plot for the P_2O_5 - B_2O_3 - ZnO - Al_2O_3 added TiO_2 glass for α of 5, 10, 15 and 20 °C/min.

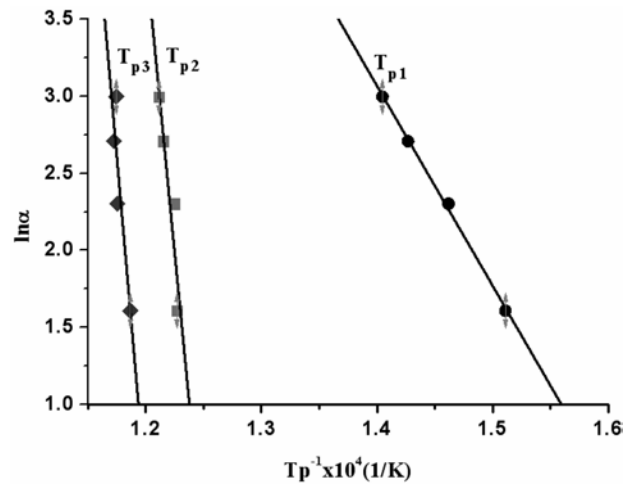


Fig. 5. Marotta plot for the P_2O_5 - B_2O_3 - ZnO - Al_2O_3 added TiO_2 glass for α of 5, 10, 15 and 20 °C/min.

Table 2. Kinetic parameters for crystallization for the P_2O_5 - B_2O_3 - ZnO - Al_2O_3 - TiO_2 glass (Calculated by the Kissinger and the Marotta method)

Temperature at the crystallization peak-maximum (°C)	Activation energy, E_c (kcal/mol)	Avrami constant (n)	Crystal growth dimension (m)
701 (T_{p1})	23	3.6	3.6
823 (T_{p2})	149	1.3	1.3
853 (T_{p3})	167	1.1	1.1

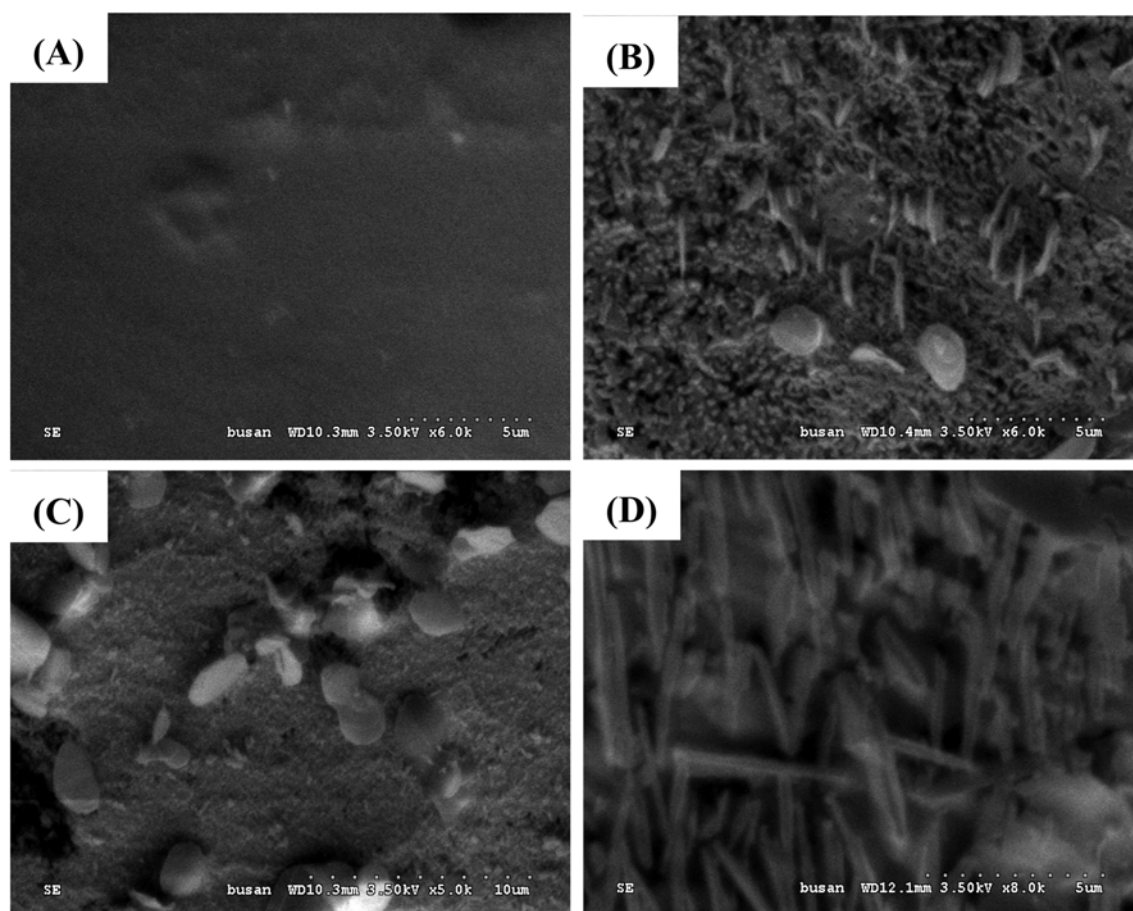


Fig. 6. SEM micrographs of samples at different heat treatment conditions at (A) 600 °C, (B) 620 °C, (C) 700 °C and (D) 840 °C for 1h, and etched at 25 °C with 1% HF for 3sec.

have an influence on nucleation density and crystallization rate [16]. The microstructure should depend on the thermal history of the specimen. Fig. 6 shows SEM micrographs of samples heated at 600 °C (A), 620 °C (B), 700 °C (C) and 840 °C (D) for 1h, respectively. The first specimen (A) had not a crystal. The second, third and forth specimens (B), (C) and (D) had microstructures composed of crystals with a relatively uniform size of 0.5-1.0 μm and 1.0-2.0 μm , respectively. Also specimens (C) and (D) had another crystal. In case of specimen (C), XRD peaks were shown weaker than specimen (D) because of incomplete crystallization.

Conclusions

From the experimental results the following conclusions can be drawn:

First, the temperature of maximum nucleation rate for α - $Ti_4P_2O_7$ and $AlPO_4$ crystals is around 720 °C, 840 °C respectively.

Second, the value of n and m depend on the crystal growth mechanism and are found to be $n = m \approx 3$ from the non-isothermal DTA measurement. The crystallization mechanism is three-dimensional growth.

Third, the apparent activation energies of crystallization

of the individual crystallites, determined using the Kissinger equalization, were in the range of 23 ± 5 kJ/mol.

Acknowledgments

This work was supported by a grant-in-aid for the National Core Research Center Program from the Ministry of Science & Technology and the Korea Science & Engineering Foundation (R15-2006-022-02001-0).

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