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Nucleation and Crystallization of Phosphate Glass for a PDP Barrier Rib by Differential Thermal Analysis

Young Seok Kim, Kyu Ho Lee, Tae Ho Kim, Young Joon Jung, and Bong Ki Ryu*

Division of Materials Science and Engineering, Pusan National University, Busan 609-735, Korea

Non-isothermal measurements with differential thermal analysis were used to study the nucleation and crystallization kinetics of P_2O_5-B_2O_3-ZnO-BaO-Al_2O_3-TiO_2 crystals in bulk glass, particularly with respect to the crystallization that occurs when the glass is heated. The temperature of the nucleation rate was determined by plotting either the reciprocal of the temperature that corresponds to the maximum crystallization peak, $1/T_p$, or the height of the crystallization peak, $(\Delta T)_p$, as a function of the nucleation temperature, T_n. The temperature at which nucleation can occur for the glass ranges from 700°C to 890°C and the temperature for the maximum nucleation is 760±5°C. The correct activation energy for the crystallization, E_c, of the glass is the same for the surface crystallization orthe bulk crystallization: namely 533 kJ/mol ± 15 kJ/mol. The analysis of the crystallization data with the Kissinger equation and the Marotta equation yields the correct value of E_c, though the crystal growth occurs only 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 ($n \approx 2$) and the dimensionality of crystal growth ($m \approx 2$).

Keywords: crystallization kinetics, phosphate glass, glass-ceramics, surface nucleation

1. INTRODUCTION

Glass-ceramic materials, which are prepared by the controlled devitrification of glass, have become established in a wide range of technical and technological applications.[1] For these applications, the following parameters of the glass should be known: the temperature range at which nucleation can occur, the temperature of the maximum nucleation rate, the activation energy, and the dimensionality of the crystal growth. A common technique for determining the nucleation rate involves heating the glass at a certain temperature for a set period so that a number of nuclei are developed within the glass.[2,3]

Differential thermal analysis (DTA) can also be used as an alternative method of determining the nucleation temperature range and the temperature of the maximum nucleation. The advantage of DTA is that it requires much less time than that needed for the classical technique and it offers more convenient descriptions for analysis of experimental data. One recent application operates with a low sintering temperature and can be applied to functional melt materials that have a non-Pb composition of glass without harmful heavy metals. To our knowledge, there has been no systematic study on the nucleation and crystallization kinetics of this type of glass; the only available data is of a preliminary nature. Our focus is on the nucleation and crystallization kinetics of the type of glass in which P_2O_5-B_2O_3-ZnO-BaO-Al_2O_3-TiO_2 crystals are precipitated when the glass is heated.

*Corresponding author: bkryu@pusan.ac.kr

2. EXPERIMENTAL PROCEDURE

The glass for this experiment had a composition of $27P_2O_5$-$23B_2O_3$-43ZnO-7BaO-$3Al_2O_3$-$6TiO_2$ (wt.%). We prepared the glass by melting a homogeneous mixture of reagent-grade P_2O_5, B_2O_3, ZnO, $BaCO_3$, Al_2O_3 and TiO_2 at 1300°C for 1 h in an alumina crucible. The melt was quenched when poured on a plate. The as-quenched glass was ground, screened with a 44 μm mesh, and then stored in an oven at 100°C to prevent moisture. To determine the temperature range of the nucleation, Tn, as well as the temperature of the maximum nucleation rate, we performed heat treatments and DTA experiments. We then placed 30 mg of the glass powder in a platinum crucible and used α-Al_2O_3 powder as a reference material. 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/min, 10°C/min, 15°C/min and 20°C/min. We then used the methods of Kissinger[4] and Marotta[5] to analyze the DTA results so that we could obtain the crystallization mode and

the activation energy values of the crystallization of each sample. All these methods were used for the purpose of obtaining more accurate kinetic parameters for the glass. To examine the phase analysis and crystallization of the heat-treated samples, we used X-ray diffraction (XRD) (Rigaku RINT 2000, Japan) and a scanning electron microscope (SEM: Jeol JSM-5400, Japan).

3. RESULTS AND DISCUSSION

As reported by Marotta *et al.*[6] and Xu *et al.*,[7] DTA can be used to determine the nucleation temperature range and the temperature of maximum nucleation. In DTA, the temperature at the maximum crystallization peak, T_p, is determined as a function of the nucleation temperature, T_n, with a constant sample weight and heating rate. Figure 1 shows typical DTA traces of the samples crystallized at heating rates of 5°C/min, 10°C/min, 15°C/min and 20°C/min. The glass transition temperature (T_g) of all curves was evidently about 575°C. The DTA curves exhibited three distinct exothermic peaks that correspond to the formation of three crystalline phases. Figure 2 shows the inverse of the temperature that corresponds to the maximum of the DTA crystallization peak, $1/T_p$, of the glass nucleated at a different T_n value for 1 h. For samples with the same composition, the following relation[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:

$$lnN = \frac{E_c}{R} \cdot \frac{1}{T_p} + constant. \quad (1)$$

The greater numbers of nuclei have a lower crystallization temperature. Thus, in Fig. 2, the change of T_p with T_n is primarily due to a change in the value of N for the glass. Furthermore, in Fig. 2, $1/T_{p1}$, $1/T_{p2}$ and $1/T_{p3}$ show where the nucleation rate reaches a maximum in the P_2O_5-B_2O_3-ZnO-BaO-Al_2O_3-TiO_2 system glass at 760°C, 890°C and 950°C, respectively. To confirm the nucleation results on the DTA curves, we conducted XRD analysis. The XRD patterns of the as-quenched glass and the glass that was heat-treated at 610°C and 700°C for 1 h have hump characteristics of an amorphous state. In contrast, as shown in Fig. 3, the glass that was heat-treated at a temperature higher than 760°C for 1 h has diffraction peaks that belong to the crystalline phase of α-$Ti_4P_2O_7$ and $AlPO_4$. The XRD peaks of the glass that was heat-treated at 700°C have a weak intensity. The DTA data were analyzed primarily with the Kissinger equation;[9] that is,

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

where α is the DTA heating rate, T_p is the crystallization

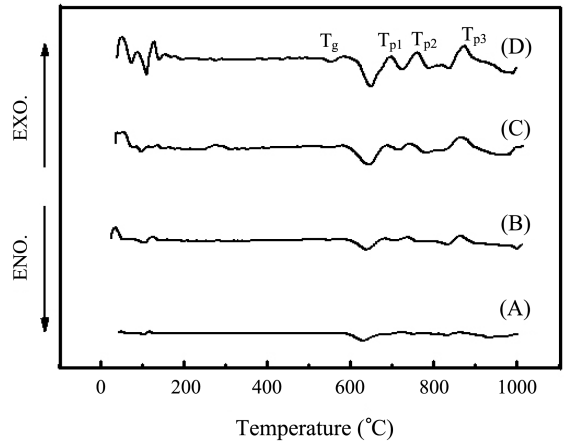

Fig. 1. DTA curves of the glass samples at heating rates of (A) 5/min, (B) 10°C/min, (C) 15°C/min, and (D) 20°C/min.

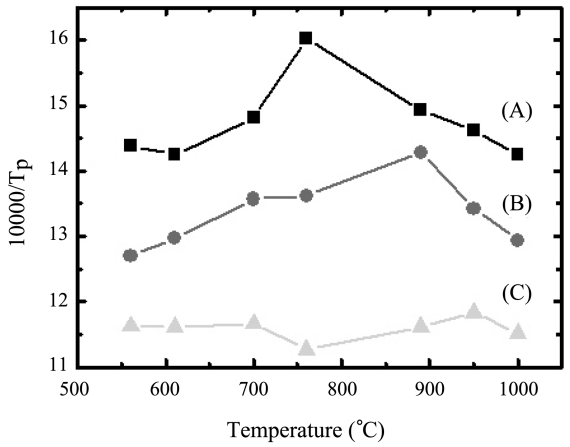

Fig. 2. Inverse of T_p for the P_2O_5-B_2O_3-ZnO-BaO-Al_2O_3-added TiO_2 glass for a particle size of <44 μm and a 30 mg sample. Each sample was held at T_n for 1 h and α = 15°C/min. (A) T_{p1}, (B) T_{p2}, and (C) T_{p3}.

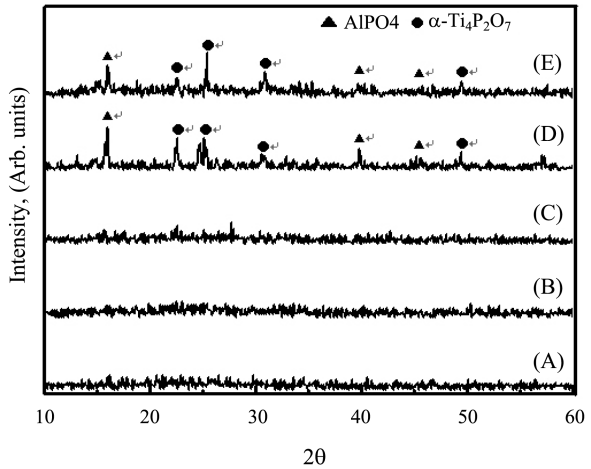

Fig. 3. XRD patterns of the P_2O_5-B_2O_3-ZnO-BaO-Al_2O_3-added TiO_2 glass for (A) as-quenched samples and (B) samples nucleated at 610°C for 1 h; (C) to (E) show samples nucleated at temperatures of 700°C (T_{p1}), 760°C (T_{p2}), and 890°C (T_{p3}) for 1 h.

peak temperature, E_{ck} is the activation energy for the crystallization, and R is the gas constant. Figure 4 shows the Kissinger plot of the glass in relation to Eq. (2), for heating rates of 5°C/min, 10°C/min, 15°C/min, and 20°C/min with the T_{p2} sample. Table 2 lists the values of E_c as determined from the slope of these plots. Matsusita and Sakka stated that Eq. (2) is valid only if crystal growth occurs on a fixed number of nuclei.[10] A sample of the maximum nucleation rate and the number of nuclei that formed during the DTA run can be regarded as negligible.[11] Therefore, Eq. (2) is applicable for the study. Matsusita and Sakka suggested the following modified form of the Kissinger equation:

$$ln\left(\frac{\alpha^n}{T_p^2}\right) = -\frac{mE_c}{RT_p} + constant, \quad (3)$$

where α is the DTA heating rate, Tp is the crystallization peak temperature, E_c is the activation energy for the crystallization, and n is the value of the Avrami constant. The value of m equals the value of n whenever crystallization at different heating rates occurs on a fixed number of nuclei. On the other hand, the number of nuclei is constant during DTA runs at different values of α. In addition, when the surface nucleation dominates, m = n = 1 and Equation.

Xu *et al*. have demonstrated that $E_{ck} = E_c$ on a fixed number of nuclei.[7] Thus, for crystal growth that occurs on a fixed number of nuclei, the analysis of DTA data with the Kissinger model (Eq. (2)) yields the correct value of E_c. The value of n can be determined as follows with the Marotta equation:[5]

$$ln\alpha = -\frac{E}{RT_p} + constant$$

$$ln\Delta T = -\frac{nE}{RT_p} + constant \quad (4)$$

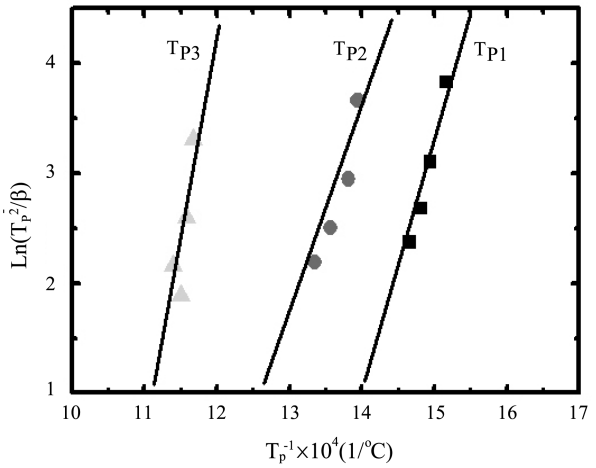

Fig. 4. A Kissinger plot for the P_2O_5-B_2O_3-ZnO-BaO-Al_2O_3-added TiO_2 glass for α values of 5°C/min, 10°C/min, 15°C/min, and 20°C/min. The sample was nucleated at 700°C for 1 h.

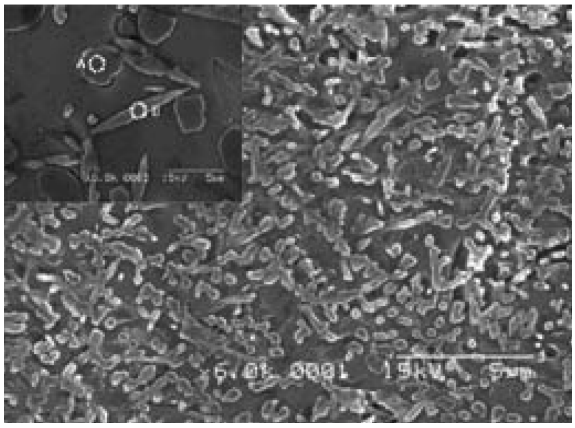

Fig. 5. A SEM micrograph of the α-Ti4P_2O_7 glass sample heated at 700°CA for 1 h.a SEM-EDS image at heat treatment condition 890°C for 1 h : (A) α-Ti4P_2O_7 and (B) $AlPO_4$.

Table 1. Kinetic parameters for the crystallization of P_2O_5-B_2O_3-ZnO-BaO-Al_2O_3-TiO_2 glass (as calculated by the Kissinger method and the Marotta method)

Temperature at the maximum crystallization peak (°C)	Activation energy, Ec (kJ/mol)	Avrami constant (n)	Crystal growth dimension (m)
675 (T_{p1})	533	2.1	2.1
737 (T_{p2})	660	1.8	1.8
877 (T_{p3})	975	1.7	1.7

Table 2. EDS element compositions of samples headed at 890°C for 1 h

element	A spherical shape (A)		A needle shape (B)	
	wt.%	at.%	wt.%	at.%
O	30.03	46.7	31.8	59.82
Al	27.28	25.15	-	-
P	27.51	22.1	6.56	6.37
Ti	1.91	0.99	32.36	20.33
Zn	13.28	5.05	29.28	13.48

where α is the DTA heating rate, T_p is the crystallization peak temperature, E is the activation energy for the crystallization, and ΔT is the deflection from the baseline of the curve. The Marotta plot of the glass according to Eq. (4), for heating rates of 5°C/min, 10°C/min, 15°C/min, and 20°C/min with T_{p2} sample (Figure is not included). As shown in Table 1, the Marotta plot indicates that the bulk crystallization is dominant in the glass. Thus, the m value of the glass becomes ≈ 2 because, as mentioned, n and m have an equal value. When allowance is made for experimental errors, the value of n is considered to be 2. Figure 5(A) shows a SEM micrograph of the glass sample heated at 700°C for 1 h. Table 2 shows that the crystals have a needle shape and a spherical shape. The EDS and XRD results show that α-$Ti_4P_2O_7$ has a needle shape and $AlPO_4$ has a spherical shape.

4. CONCLUSIONS

From the experimental results, we have drawn three conclusions. Firstly, the temperature of the maximum nucleation rate is around 760°C for the α-$Ti_4P_2O_7$ crystals and around 890°C for the $AlPO_4$ crystals. Secondly, from the non-isothermal DTA measurements, we can deduce that the value of n and m, which depends on the crystal growth mechanism, can be expressed as $n = m \approx 2$. Note also that the crystallization mechanism yields two-dimensional growth. Finally, from the Kissinger equation, we determined that the crystallization activation energy of an individual crystalline is 533 kJ/mol ±15 kJ/mol.

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