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KINETICS OF NON-ISOTHERMAL CRYSTALLIZATION OF SOME FLUOROZIRCONATE GLASSES

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ABSTRACT

The non-isothermal crystallization kinetics of ZrF_4-BaF_2 and ZrF_4-BaF_2-NaF-AlF_3 glasses was studied on the basis of the method for determining the activation energy for crystal growth from DSC curves of various heating rates. It was found that the rate of crystal growth in ZrF_4-BaF_2 glasses was shown to be controlled by viscosity of glasses and that the rate of crystal growth in ZrF_4-BaF_2-NaF-AlF_3 glasses was controlled by diffusion.

INTRODUCTION

Thermal analysis is a very useful tool for studying the kinetics of crystallization of glass as it is a rapid and convenient means. Methods for analyzing the non-isothermal crystallization were proposed on the basis of nucleation and growth process without the prior assumption of the validity of Johnson-Mehl-Avrami equation which was derived for isothermal crystallization [1-3]. MacFarlane et al [4] derived the almost similar expression for the crystallization in which the crystal growth rate is controlled by diffusion. These are expressed as [1-4]

$$\ln[-\ln(1-x)] = -n \ln\alpha - 1.052m \frac{E_a}{RT} + \text{Const.} \qquad (1)$$

where x is the volume fraction of crystals precipitating in a glass heated to a temperature, T, at a constant rate, α, E is the activation energy for crystal growth and n and m are numerical factors depending on crystallization mechanism. The values of n and m for various crystallization mechanisms are shown in Table 1.

In recent years, much attention has been attracted to the fluoride glasses based on ZrF_4 and BaF_2 because of the potential uses in numerous optical applications [5,6]. Only a few studies [4,7-11], however, have been reported on the crystallization behaviors

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TABLE 1

Values of n and m for various crystallization mechanisms.

	Growth controlled by interface reaction		Growth controlled by diffusion	
	n	m	n	m
Bulk nucleation with varying number of nuclei*1)				
3-dimensional growth	4	3	2.5	1.5
2-dimensional growth	3	2	2	1
1-dimensional growth	2	1	1.5	0.5
Bulk nucleation with constant number of nuclei*2)				
3-dimensional growth	3	3	1.5	1.5
2-dimensional growth	2	2	1	1
1-dimensional growth	1	1	0.5	0.5
Surface nucleation	1	1	0.5	0.5

*1) The number of nuclei is inversely proportional to the heating rate.
*2) The number of nuclei does not change with the heating rate.

of the fluoride glasses. In the present study, the crystallization kinetics of some fluoride glasses was investigated by the non-isothermal analysis and the activation energies for crystal growth were determined from DSC measurements. The growth mechanisms were discussed.

EXPERIMENTAL

Glasses used in this study are ZrF_4-BaF_2 and ZrF_4-BaF_2-NaF-AlF_3 systems. Raw materials used were high purity fluorides. Batches producing 25g glass with addition of 10g $NH_4F\cdot HF$ were placed in platinum crucibles and put into an electric furnace preheated at 400°C. The batches were then heated to 900°C and kept at this temperature for 10 min. The melts of ZrF_4-BaF_2-NaF-AlF_3 system were cast onto a steel plate, and those of ZrF_4-BaF_2 system were quenched rapidly using a twin roller. All operations were made under N_2 gas atmosphere.

The DSC measurements were made under Ar gas flow with a Rigaku Denki thermal analysis apparatus which has a platinum sample holder of 4 mm inner diameter and 2 mm depth. The viscosity of ZrF_4-BaF_2-NaF-AlF_3 glasses was measured by a penetration method in the range of 10^7 - 10^{11} poises using a Rigaku Denki thermomechanical analysis apparatus. It was impossible to measure the viscosity of ZrF_4-BaF_2 glasses because glass specimens are so thin.

The crystals precipitated in the glasses were identified by the

X-ray diffraction analysis and the morphology of the crystals were observed with a polarized optical microscope.

RESULTS

Fig.1 shows the logarithmic viscosity of ZrF_4-BaF_2-NaF-AlF_3 glasses as a function of reciprocal temperature. It is seen that the viscosities obey the Arrhenius type equation

$$\eta = A \exp\left(\frac{E_\eta}{RT}\right) \qquad (2)$$

where E_η is the activation energy for viscous flow. The activation energies, E_η, are shown in Table 2. The E_η-values in the present study are almost same to those of similar fluoride glasses measured by Tran et al [12,13].

Fig.2 shows the DSC curves of ZrF_4-BaF_2 binary glasses heated at 1 K/min. The samples were 50-80 mg glass flakes of 200-300 μm thickness. The sharp exothermic peaks in each curve were confirmed to be caused by crystallization of glass. When the BaF_2 content is higher than 45 mol%, the main crystalline phase was ß-$BaZrF_6$, and when the BaF_2 content is lower than 35 mol%, the main crystalline phase was ß-$BaZr_2F_{10}$. Similar DSC curves of ZrF_4-BaF_2-NaF-AlF_3 glasses were obtained using the samples of 90 mg glass particles passing through a sieve of 149 μm openings and remaining on that of 125 μm openings. The main crystalline phase precipitating first was confirmed to be ß-$BaZrF_6$.

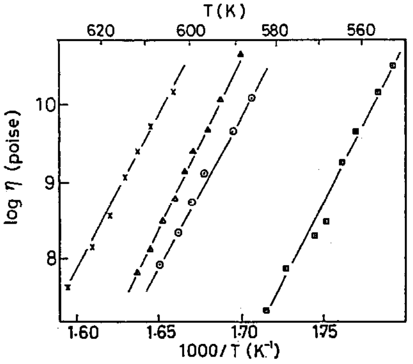

Fig.1. Viscosity of ZrF_4-BaF_2-NaF-AlF_3 glasses as a function of reciprocal temperature.
×:No.5 △ :No.6 ○:No.7
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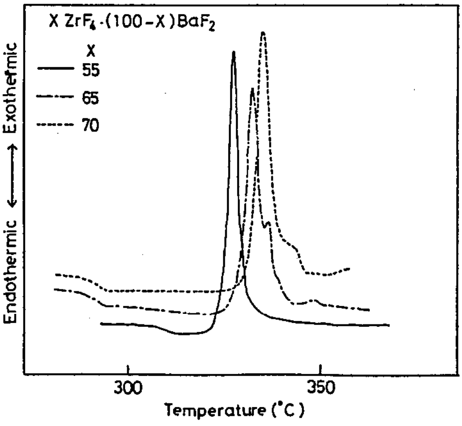

Fig.2. DSC curves of ZrF_4-BaF_2 glasses with a heating rate of 1 K/min.

DISCUSSION

ZrF_4-BaF_2 glasses.

Since glassy state is a thermodynamically non-equilibrium state, the glass transition temperature, T_g, and the crystallization temperature, T_c, are the important factors for evaluating the stability of the glassy state. Fig.3 shows the variation of T_g and T_c of ZrF_4-BaF_2 glasses heated at 2 K/min with composition. It is seen that the value of $(T_c - T_g)$ is large around the composition of 30-40 mol% BaF_2, indicating that the glasses of this composition range are most stable. It is also seen that the T_c and T_g increase rapidly as the composition reaches to 50 mol% BaF_2. This phenomenon is supposed to be related with the change of the coordination number of F^- anions around Zr^{4+} cation [7,14-16].

When a glass specimen is heated at a heating rate, α, the volume fraction of crystal increases with temperature, obeying the equation (1). By plotting $\ln[-\ln(1-x)]$ against $\ln\alpha$ at a fixed temperature, the n-value was determined to be 2-3 depending on the sample thickness. From the optical microscopic observations, it was found that the number of crystal particles does not change with heating rate. This means that the number of crystal nucleous is constant, not depending on the heating rate, and, accordingly, n should be equal to m (see Table 1).

Fig.4 shows the plot of $\ln\alpha$ against the reciprocal of peak temperature of DSC curve. It

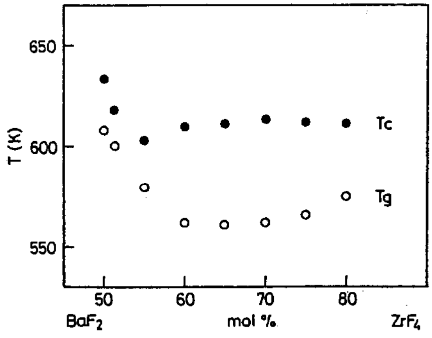

Fig.3. Variation of glass transition temperature and crystallization temperature of ZrF_4-BaF_2 glasses obtained from DSC curves with a heating rate of 2 K/min.

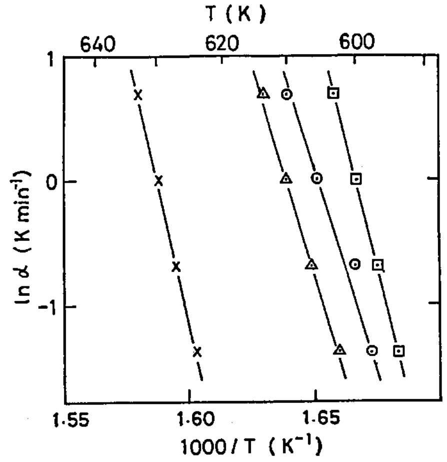

Fig.4. Relation between natural logarithm of heating rate and reciprocal of peak temperature in DSC curve of ZrF_4-BaF_2 glasses. × :No.1 □ :No.2 ○ :No.3 △ :No.4

TABLE 2

Composition and activation energies for crystal growth and viscous flow.

	Composition (mol%)				E_a	
	ZrF_4	BaF_2	NaF	AlF_3	(kcal/mol)	
No.1	50	50			172	
No.2	55	45			165	
No.3	60	40			128	
No.4	70	30			138	
					$(m/n)E_a$	E_η
No.5	50	40	2	8	115	186
No.6	50	36	6	8	121	206
No.7	50	28	14	8	120	181
No.8	50	24	18	8	111	192

is already known that the crystal volume fraction at peak temperature is almost same irrespective of the heating rate [2]. Therefore, the slopes of the straight lines in Fig.4 give the activation energy, E_a, for crystal growth directly. The E_a values thus obtained are shown in Table 2. In the glasses containing 45 and 50 mol% BaF_2, the main crystalline phase precipitated is ß-$BaZrF_6$, and in the glasses containing 30 and 40 mol% BaF_2, the main crystalline phase is ß-$BaZr_2F_{10}$. It is seen that the activation energy for crystal growth, E_a, increases rapidly as the composition reaches to 50 mol% BaF_2, being similar trend to that of the glass transition temperature. This suggests that the rate of crystal growth is controlled by viscosity, although no data on viscosity of this system are available.

ZrF_4-BaF_2-NaF-AlF_3 glasses

In this four-component system, the composition of the precipitating crystal is much different from that of the mother phase than in the former two-component system. Fig.5 shows the relation between the lnα and the peak temperature. According to equation (1), these straight lines give $(m/n)E_a$. The $(m/n)E_a$ thus determined are shown in Table 2. The n-value was determined to be 2-3 by the plot of ln[-ln(1-x)] at a certain temperature against lnα, while the m-value could not be determined because the glass

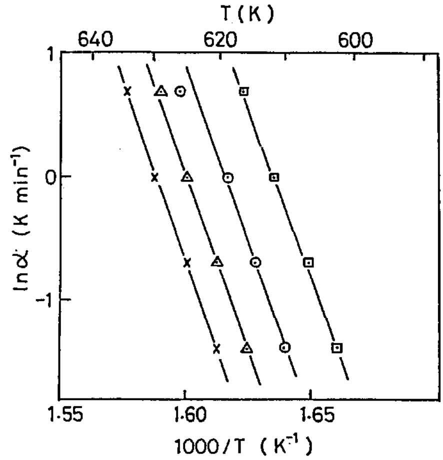

Fig.5. Relation between natural logarithm of heating rate and reciprocal of peak temperature in DSC curve of ZrF_4-BaF_2-NaF-AlF_3 glasses. X:No.5 △:No.6 O:No.7 □:No.8

particles were used as samples. Since the contribution of surface nucleation increases as the surface area increases [2,17], it is thought that the (m/n) should be close to 1 and $(m/n)E_a$ should be close to E_a. It is seen, therefore, that the activation energies for crystal growth seem remarkably small compared with those for viscous flow, and it is supposed that the rate of crystal growth is controlled by diffusion of some component, not by the viscosity of glass.

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