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Devitrification studies of the $PbO–ZnO–B_2O_3$ glass system with added SiO_2, $BaTiO_3$ and NiO_2 [1]

Jinn-Shing Lee [a,b], Tsung-Huang Lee [a], Chin-Wang Huang [b] and Wei-Ping Pan [c]

[a] *P.O. Box 90008-15-9, Chung Shan Institute of Science and Technology, Long-Tan, 32526 (Taiwan, ROC)*
[b] *Department of Chemistry, Chung Yuan Christian University, Chung-Li, 32023 (Taiwan, ROC)*
[c] *Department of Chemistry, Western Kentucky University, Bowling Green, KY 42101 (USA)*

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Abstract

The devitrification mechanism of the glass system $PbO–B_2O_3–ZnO$ was studied using non-isothermal techniques. Experimental results show that the devitrification mechanism of the glass system $PbO–B_2O_3–ZnO$ with added SiO_2 is virtually bulk nucleation controlled, but that surface nucleation occurs when NiO_2 or $BaTiO_3$ is added to $PbO–B_2O_3–ZnO$ glass.

INTRODUCTION

Crystallized solder glasses are an example of sintered glass-ceramics [1,2]. It has been shown that a solder glass in the system $PbO–B_2O_3–ZnO$ is not capable of forming a glass-ceramic structure in monolithic form but does form such a structure after milling, owing to the surface nucleation character of its crystallization.

Glasses in the system $PbO–B_2O_3–ZnO$ with small amounts of SiO_2, Al_2O_3, BaO etc. [3] are often used to seal the substrates at around 450°C. These glasses which devitrify during the sealing operation form glass-ceramic composites [4] having a lower thermal expansion coefficient than the parent vitreous glass.

Hence the purpose of the present work was to characterize the mechanism of crystallization of $PbO–B_2O_3–ZnO$ solder glass by examining the effect of small admixtures in this glass on the DTA curves.

Correspondence to: J.S. Lee, P.O. Box 90008-15-9, Chung Shan Institute of Science and Technology, Long-Tan, 32526, Taiwan, ROC.

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EXPERIMENTAL

The glasses with the compositions listed in Table 1 were prepared by melting analytical grade reagents at 1100°C in a platinum crucible in an electric furnace for 2 h, and casting them in graphite molds at a high cooling rate. The quenched glasses were crushed very carefully using a stainless steel pestle and mortar, and then sieved in order to obtain a coarse powder of between 30 and 50 mesh. The glass powder below 50 mesh was ground again in an agate mortar, and then shifted to separate the fine particle size (pass 325 mesh).

The DTA curves of each approximately 30 mg sample of fine or coarse glass powder were recorded in air at different heating rates (2–20°C min^{-1}). A Rikagu-Denki thermoanalyzer (model 8121) was used, and powdered α-Al_2O_3 was used as a reference material.

A Philips PW 1920/00 X-ray powder diffractometer and a Hitachi scanning electron microscope were employed in this study.

RESULTS AND DISCUSSION

The activation energy E and the parameter m were calculated from the DTA curves using eqns. (1–3):

$$\ln h = -E/RT_p + \text{constant} \quad (1)$$

$$\ln h/T_p^2 = -E/RT_p + \text{constant} \quad (2)$$

$$\ln \Delta T = -mE/RT_p + \text{constant} \quad (3)$$

where the parameter m depends on the mechanism and morphology of the devitrification, and the deflection from the baseline ΔT is proportional to the instantaneous reaction rate. Equations (1) and (2) are based on the shift of the crystallization peak temperature T_p as the heating rate h is changed. Equation (3) is based on the assumption that the initial part of the crystallization peak has a much larger effect on the ΔT deflection than the volume fraction devitrified. The DTA curves of the glass system PbO–B_2O_3–ZnO with added SiO_2, $BaTiO_3$ and NiO_2 are shown in Fig. 1.

TABLE 1

Weight percentage composition of glasses

Glass	PbO	B_2O_3	ZnO	SiO_2	NiO_2	$BaTiO_3$
H	80	8	12	5		
I	80	8	12		5	
J	80	8	12			5
K	80	8	12			

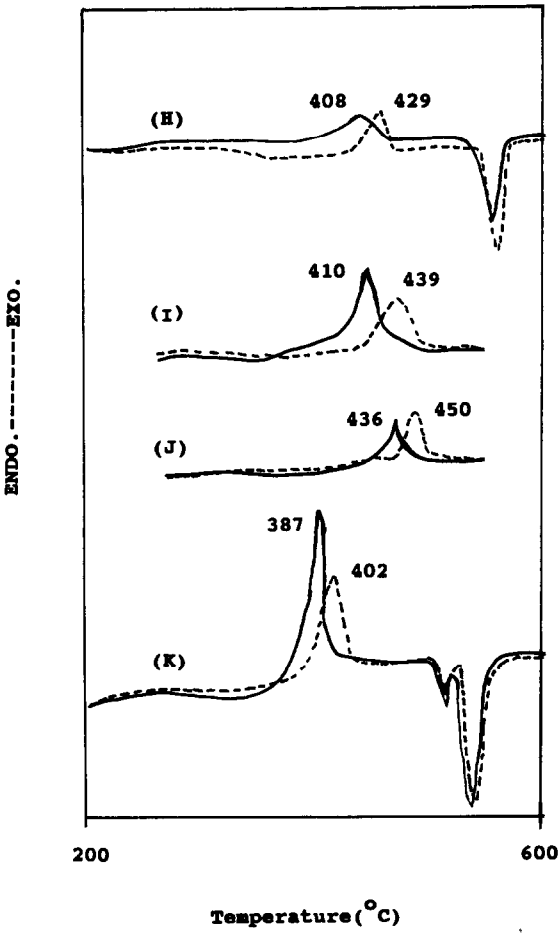

Fig. 1. DTA curves of glass with additions of coarse and fine glass powders. The solid lines represent −325 mesh powder, and the broken lines represent the powder between 30 and 50 mesh.

The values of the kinetic parameters E and m were calculated from the slope using eqns. (1)–(3) and are reported in Tables 2 and 3. The value of m suggests that surface devitrification takes place when $BaTiO_3$ or NiO_2 is added to $PbO–B_2O_3–ZnO$ glass, but that bulk devitrification occurs when SiO_2 is added to $PbO–B_2O_3–ZnO$ glass.

The electron micrographs of the $PbO–B_2O_3–ZnO$ glass system with small additions of SiO_2, $BaTiO_3$ and NiO_2, are shown in Figs. 2–4. The crystalline phases are different in each case, especially with NiO_2 added to $PbO–B_2O_3–ZnO$ glass. The X-ray diffraction patterns for the $PbO–B_2O_3–ZnO$ glass system with added SiO_2, $BaTiO_3$ and NiO_2 are shown in Fig. 5. X-ray diffraction patterns indicate that the crystalline phases are virtually absent, except when NiO_2 is added to $PbO–B_2O_3–ZnO$ glass. These

TABLE 2

Kinetic parameters for $PbO-B_2O_3-ZnO$ glasses with additions of a fine powder

Glasses	E_1 [a] (kcal mol^{-1})	E_2 [b] (kcal mol^{-1})	E_{ave} (kcal mol^{-1})	mE (kcal mol^{-1})	m
H	53.71	51.01	52.36	106.78	2.04
I	56.05	53.44	54.75	82.91	1.51
J	84.15	81.47	82.81	114.42	1.38
K	64.4	61.57	62.99	51.87	0.82

[a] Activation energy calculated by plotting ln h vs. $(1/T_p)\times 1000$.
[b] Activation energy calculated by plotting $\ln(h/T_p^2)$ vs. $(1/T_p)\times 1000$.

Fig. 2. Electron micrograph of H glass after heat treatment.

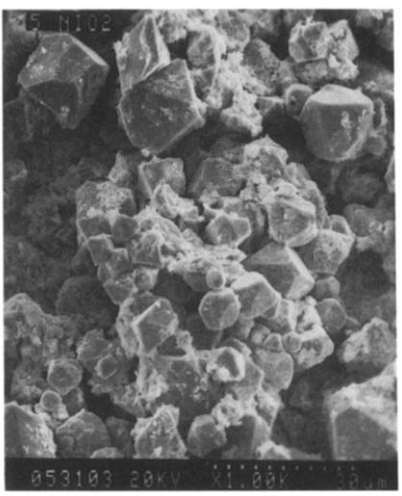

Fig. 3. Electron micrograph of I glass after heat treatment.

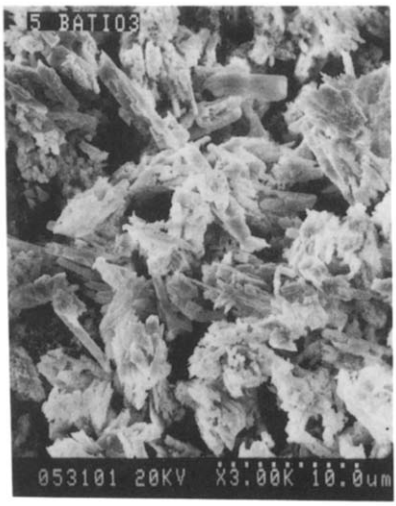

Fig. 4. Electron micrograph of J glass after heat treatment.

results are consistent with the work of Rabinovich [9]: "Addition of SiO_2 and Al_2O_3 permits reduction of the crystallizing tendency of $PbO–B_2O_3–ZnO$ glasses."

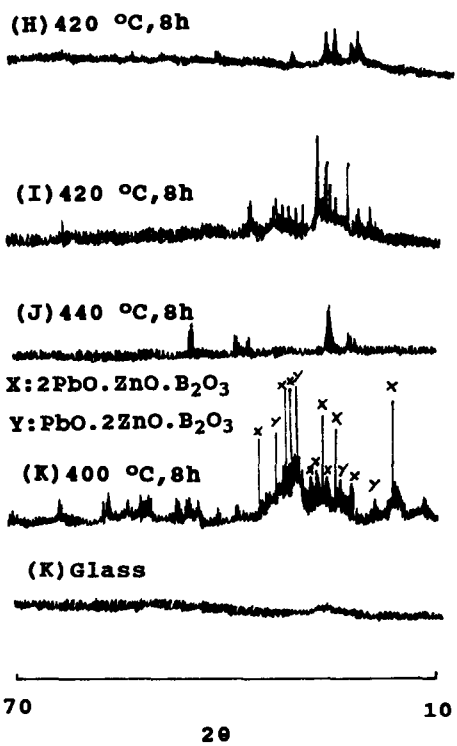

Fig. 5. X-ray diffraction patterns of the glasses.

TABLE 3

Kinetic parameters for $PbO–B_2O_3–ZnO$ glasses with additions of a coarse powder

Glasses	E_1 [a] (kcal mol^{-1})	E_2 [b] (kcal mol^{-1})	E_{ave} (kcal mol^{-1})	mE (kcal mol^{-1})	m
H	59.78	57.31	58.55	80.14	1.37
I	45.29	43.08	44.19	47.15	1.08
J	73.89	71.24	72.57	90.98	1.25
K	47.17	44.51	45.34	66.82	1.47

[a] Activation energy calculated by plotting ln h vs. $(1/T_p)\times 1000$.

[b] Activation energy calculated by plotting $\ln(h/T_p^2)$ vs. $(1/T_p)\times 1000$.

CONCLUSION

From the experimental results, it can be concluded that the devitrification mechanism of the $PbO–B_2O_3–ZnO$ glass is changed by adding oxide, especially SiO_2, and that the crystallizing tendency of $PbO–B_2O_3–ZnO$ glass is reduced by adding small amounts of SiO_2, $BaTiO_2$ and NiO_2.

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