

Phase separation of $\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5$ glasses induced by polarization in an electric field

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The electromagnetic theory is used to characterize the polarization processes in glasses. At low B_2O_3 content, the electric field treatment inhibits the phase separation of the glass. But, at low P_2O_5 content, electric field treatment promotes the process. The analysis shows that the free energy may be reduced or enhanced by the electric field depending on the ratio of the dielectric constants of the old and new phases. This means that the electric field can either stimulate or inhibit the nucleation process. The theory is in excellent agreement with the experimental results. And, we may extend it to the phase transformation of all dielectric materials applying an electric field. These results suggest a possible method for the preparation of nanophase glass-ceramics. © 2000 Kluwer Academic Publishers

1. Introduction

A wide variety of binary or multicomponent systems, both organic and inorganic, exhibit liquid-liquid immiscibility and tend to separate into two or more liquid phases over a well defined range of composition and temperature. The phenomenon has been known for many years in glass-forming oxide systems, particularly those based on silica and boric oxide. Interest in metastable immiscibility has been stimulated by the discovery and development of glass-ceramics, materials made by the controlled crystallization of glasses. Thus it has been found that liquid separation is often the precursor to crystal nucleation and growth in certain glass-ceramics compositions and can profoundly influence the crystallization path of a system on the phase diagram. For this reason, the influence of phase separation on crystallization has been extensively studied, with particular attention directed to its effect on crystal nucleation [1–4].

In recent years there have been numerous studies of the nucleation and crystallization of glasses, and many glass-ceramics materials prepared by the controlled crystallization have been developed with a variety of properties and applications, including in the medical and dental field, in the sealing materials field, and in the structural materials field [5–7]. Much progress has also been made in the area of glass-ceramics in order to improve the properties of glass-ceramics.

Evidence of a pronounced effect by electric field on the kinetics of phase separation has been provided by studies [8, 9]. In the investigation, a marked acceleration of separation in a complex silicate glass is noted for low frequency fields of modest intensities, but no attempt were made to investigate systematically the effect of electric field on phase separation. In this paper, phase separation of glasses in the presence of an electric field is investigated. The objects are to study the mech-

anism of phase separation under an electric field, then further prepare nanometer glass-ceramics by control of phase separation of glasses.

2. Model of phase separation of glass applying an electric field

2.1. Variation in energy of glass by electric field

The initial energy of glass, representing the total work done in establishing the initial field, is obtained by evaluating all space [10]

$$U_1 = \frac{1}{2} \int_V E_1 D_1 dV \quad (1)$$

Where E_1 is the electric field strength, V is the volume of glass.

After the production of phase separation in glass the modified field at any point is E , and the difference $E_2 = E - E_1$ is thus the field resulting from the polarization of the body. The volume occupied by the particle of phase separation we denote by V_1 (ϵ_2 is dielectric constant), that of the medium exterior to it by V_2 (ϵ_1 is dielectric constant). The energy of the field owing to phase separation of glass is

$$U_2 = \frac{1}{2} \int_V E D dV \quad (2)$$

If at every point ϵ_2 is increased owing to phase separation of glass, the consequent variation in the electric energy will be equal to

$$\delta U = -\frac{1}{2} \int \delta \epsilon E E_1 dV = -\frac{1}{2} \int \delta \epsilon E^2 dV \quad (3)$$

Therefore, the change in energy resulting from phase separation of glass is

$$U = -\frac{1}{2} \iint_{\varepsilon_1}^{\varepsilon_2} E^2 d\varepsilon dV \quad (4)$$

2.2. Mechanism of phase separation of glass by electric field

The change in free energy required for the formation of a cluster in an externally applied uniform direct current electric field is

$$\Delta G = \Delta G_0 + \Delta G_E \quad (5)$$

Where ΔG_0 is the same free energy in the absence of the electric field, and ΔG_E is the free energy change owing to the electric field.

The free energy change without an electric field on forming the nucleus is containing surface energy and strain energy [11]

$$\Delta G_0 = \frac{4}{3}\pi\gamma^3\Delta G_V + 4\pi\gamma^2\sigma \quad (6)$$

Where γ is a nucleus size, ΔG_V is strain energy per unit volume, and σ is effective surface free energy per unit area.

According to (4), the free energy of the electric field before the phase separation and after that is

$$\Delta G_E = -\frac{1}{2}E^2(\varepsilon_2 - \varepsilon_1)\frac{4}{3}\pi\gamma^3 \quad (7)$$

The change of free energy owing to the phase separation of glass in the presence of the electric field has the form shown in (8)

$$\Delta G = \frac{4}{3}\pi\gamma^3 \left[\Delta G_V - \frac{1}{2}E^2(\varepsilon_2 - \varepsilon_1) \right] + 4\pi\gamma^2\sigma \quad (8)$$

The variation of ΔG with γ is

$$\frac{\partial \Delta G}{\partial \gamma} = 4\pi\gamma^2 \left[\Delta G_V - \frac{1}{2}E^2(\varepsilon_2 - \varepsilon_1) \right] + 8\pi\gamma\sigma = 0 \quad (9)$$

The critical nucleus size is

$$\gamma_c = \frac{2\sigma}{|\Delta G_V| + (1/2)E^2(\varepsilon_2 - \varepsilon_1)} \quad (10)$$

The maximum free energy forming a critical nucleus size is

$$\Delta G_c = \frac{16\pi\sigma^3}{3[|\Delta G_V| + (1/2)E^2(\varepsilon_2 - \varepsilon_1)]^2} \quad (11)$$

Formula 10 and 11 show the effect of field intensity (E^2) and dielectric constants ($\varepsilon_2 - \varepsilon_1$) on a critical nucleus size and free energy of phase separation. Hence if $\varepsilon_2 > \varepsilon_1$, γ_c and ΔG_c are reduced and nucleus formation or phase separation of glass is encouraged by the application of the electric field, however, if $\varepsilon_2 < \varepsilon_1$ it is inhibited. Following the increase in electric field intensity, the promoted (or retarded) nucleus is due to the decrease (or increase) in γ_c and ΔG_c .

TABLE I Compositions of glasses containing B_2O_3 (mol%)

	CBP1	CBP2
B_2O_3	10	90

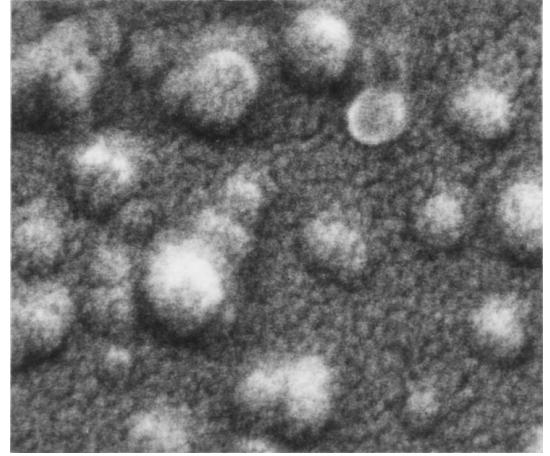


Figure 1 Morphology of phase separation of CBP1 glass (610°C × 60 min × 4 kv/cm).

3. Experimental results and discussion

3.1. Experimental method

P. F. James *et al.* [7] investigate the glasses prepared from reagent-grade calcium hydrogen phosphate, $CaH_4(PO_4)H_2O$, and boric acid, H_3BO_3 . The mole ratio CaO/P_2O_5 is kept equal to unity and B_2O_3 content is varied from 0 to 45 mol%. Then, the morphology of calcium-boric-rich particles is produced by a nucleation and growth mechanism. Increasing B_2O_3 content to 90%, the particles of phase separation of the glass are rich in phosphate-calcium content [12]. Therefore, we design compositions of glasses as shown in Table I.

CBP1 and CBP2 ($CaO \cdot B_2O_3 \cdot P_2O_5$) glass systems were made at 1200 °C–1350 °C for 2 h, and the specimens were annealed at 400 °C for 1 h. After being processed into 10 × 10 × 5 mm samples, the glasses are heat treated in the presence of an electric field or not. The specimens were heat-treated at 610 °C for 60 min in different electric field strengths. The distribution of phase separation particles of glasses is observed by S-4200SEM.

3.2. Results and discussion

3.2.1. B_2O_3 content

Fig. 1 shows micrographs of specimen of CBP1 glass which is treated at 610 °C for 60 min in the presence of the electric field (4 kv/cm). The phase separated particles is few. This implies that the electric field treatment inhibits the phase separation of CBP1 glass compared with the heat treatment in the absence of an electric field (610 °C × 60 min) (Fig. 2).

Fig. 3 shows the morphology of phase separation of CBP2 glass in the presence of the electric field ($E = 4$ kv/cm), and accelerated nucleation is observed in the microstructure in contrast to that in the absence of an electric field (Fig. 4).

The dielectric constant of phase separation particles increases with the B_2O_3 content. For the CBP1 glass

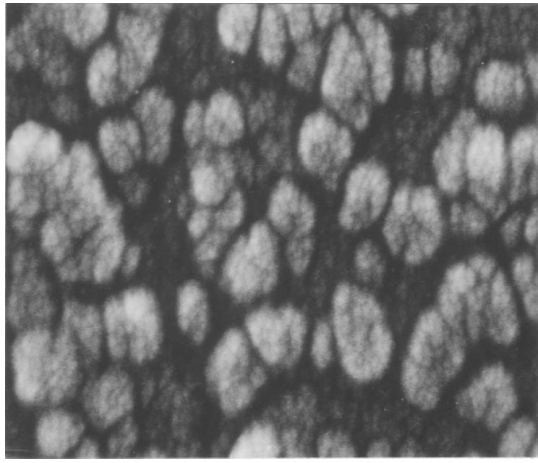


Figure 2 Morphology of phase separation of CBP1 glass (610°C × 60 min).

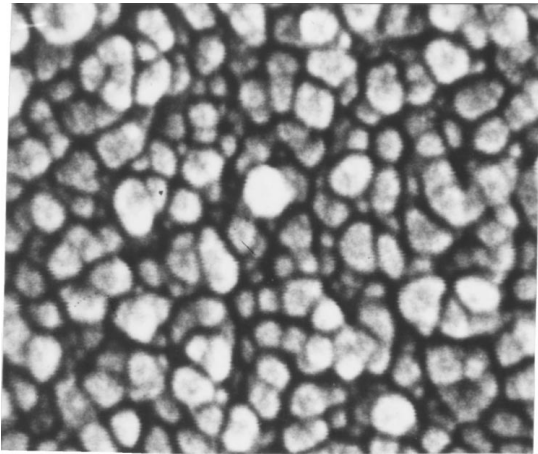


Figure 3 Morphology of phase separation of CBP2 glass (610°C × 60 min × 4 kv/cm).

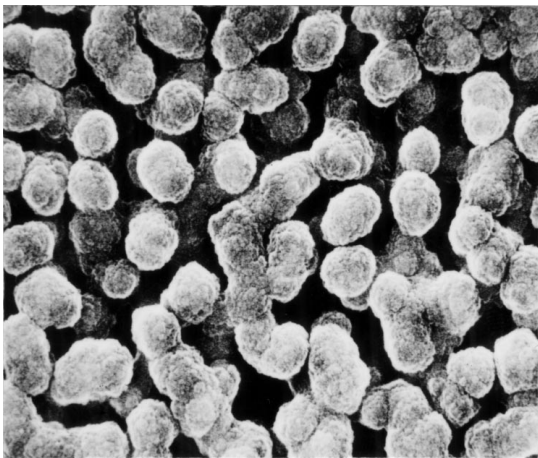


Figure 4 Morphology of phase separation of CBP2 glass (610°C × 60 min).

system, the phase separation particles are rich in Boron and Calcium contents. As shown in Table II, the dielectric constant of phase separation particles is smaller than that of the glass matrix ($\epsilon_2 < \epsilon_1$). So γ_c and ΔG_c are increased, which means that the electric field treatment inhibits the phase separation of the glass. As the results of applying an electric field, there are few phase separated particles in the glass matrix. For CBP2 glass,

TABLE II Dielectric constants of solid substances [13]

Materials	P ₂ O ₅	B ₂ O ₃	CaO	CBP2	CBP1
Dielectric constants	15.8–67.4	4.5–6.2	10–12	5–9	14.3–16.8

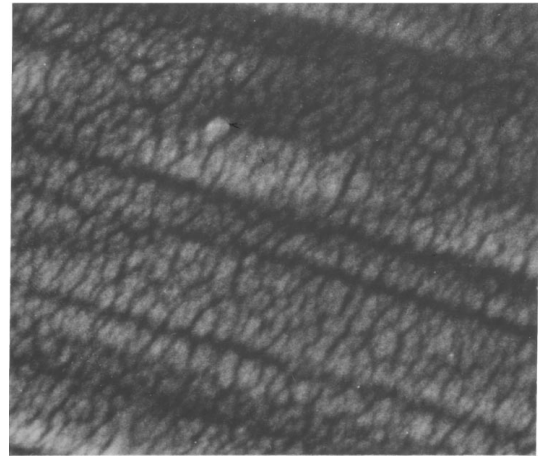


Figure 5 Morphology of phase separation of CBP1 glass (610°C × 60 min × 10 kv/cm).

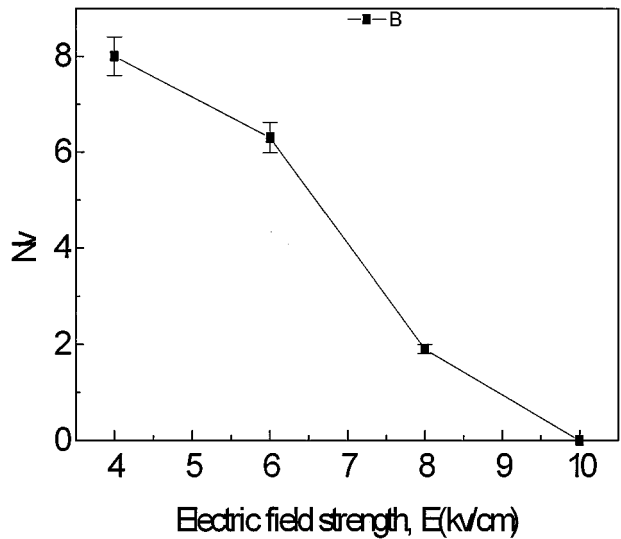


Figure 6 Number of phase separation particles vs electric field strength.

as shown in Table II, the dielectric constant of phase separation particles is larger than that of the glass matrix ($\epsilon_2 > \epsilon_1$). Therefore, as shown in formula 10 and 11, γ_c and ΔG_c are reduced. This implies that the electric field treatment promotes the phase separation of CBP2 glass.

3.2.2. Electric field strength

As the results of increasing the electric field ($E = 10$ kv/cm) (Fig. 5), phase separation of CBP1 glass is significantly inhibited so that no phase separation is found in the microstructure of glass. With the increase in the electric field strength, owing to greater γ_c and ΔG_c , the phase separation is not produced in the glass matrix.

Fig. 6 shows the number of nucleation per unit volume plotted against electric field strength at 610°C for 60 min (CBP1 glass). The N_v values are obtained from

the micrographs using the analysis method [7]. The overlap nucleation introduces uncertainties in the N_v values for CBP1 glass by the electric field (Fig. 1). Owing to the increase in the electric field strength, there is a clear decrease in γ_c and ΔG_c , so it leads to the decrease in N_v .

Therefore, by adding different compositions in glasses, dielectric constants of glasses may change. We can prepare nanophase glass-ceramics by control of phase separation of glasses applying an electric field [12].

4. Conclusions

1. For the CBP1 glass system the electric field treatment inhibits the phase separation, but for the CBP2 glass system it promotes the phase separation. Increasing the electric field strength, the effect of the electric field on the phase separation is greatly increased.

2. Formula based on electromagnetic theory reveals the effect of electric field on phase separation of glasses. When the dielectric constant of phase separation particles is larger than that of the glass matrix ($\varepsilon_2 > \varepsilon_1$), the electric field treatment induces phase separation, but if $\varepsilon_2 < \varepsilon_1$ it is inhibited.

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