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Phase separation of $CaO{\cdot}Al_2O_3{\cdot}SiO_2$ glasses induced by electric field

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By means of S-4200 SEM, phase separation of $CaO\text{-}Al_2O_3\text{-}SiO_2$ glasses upon application of an electric field is investigated. The experimental results show that externally applied electric field promotes the phase separation of the glass, and it leads to a different size of the droplet phase. In the vicinity of the anode of the glass, the smaller droplet phase is induced compared with the cathode of the glass. The accelerating phase separation of the glass in the presence of an electric field is due to the decrease in the free energy forming a critical nucleus size. The different size of the droplet phase of the cathode is due to the increase in the driving force of nucleation and decrease in the viscosity of the glass compared with that of the anode of the specimen. © *1999 Kluwer Academic Publishers*

1. Introduction

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 [1–3]. Much progress has also been made in the area of glass-ceramics in order to improve the properties of glass-ceramics.

In many instances, glass-ceramics are able to tailor the properties of the materials through control of phase separation, completeness of crystallization, and phase morphology. It is now well established that liquid-liquid phase separation can substantially influence the course of crystallization of glasses. Such effects are particularly important in the formation of many glass-ceramic bodies, and phase separation has long been considered an important precursor step in promoting the required copious nucleation. For this reason, the influence of phase separation on crystallization has been extensively studied, with particular attention directed to its effect on crystal nucleation [4–7].

Evidence of a pronounced effect by electric field on the kinetics of phase separation has been provided by the previous studies [8, 9]. In these studies, a marked acceleration of phase separation in a complex silicate glass is noted for low frequency fields of modest intensities, but no attempt has been made to investigate systematically the effect of electric field on phase separation. In present work, the phase separation of a glass subjected to an electric field is investigated. The objective is to study the mechanism of phase separation under an electric field, then further prepare nanometer glass-ceramics by controlled phase separation in the glass.

2. Experimental

Glass system containing (10–20 mol %)CaO·(10–15 mol %)Al_2O_3·(60–70 mol %) SiO_2, 8 mol % TiO_2 and 10 mol % alkali was melted at 1450 °C for 2 h, and then cast onto a stainless steel plate. The resulting glasses were annealed at 600 °C for 1 h (no phase separation, i.e., uniform glasses). The heat-treatment temperature was chosen on the basis of the DTA analysis, which exhibited the glass transition temperature at about 680 °C. After being processed into $10 \times 10 \times 5$ mm samples, the glass was heat-treated at 700 °C for 10 min in the presence of an electric field or not. The specimens treated in the presence of an electric field are either morphous or amorphous by means of X-ray diffraction (XRD) (Fig. 4). The specimens were polished, and etched for up to 80 s in a $1HF{\cdot}99H_2O$ (vol %) solution. The morphology of droplet phase was observed by S-4200SEM.

In order to investigate the droplet phase and matrix phase of the CAS glass, energy-dispersive electron microanalysis (EDAX) was used.

3. Experimental results

Fig. 1 shows the micrographs of droplet phase of CAS glass treated at 700 °C for 10 min. Fig. 2 shows the morphology of droplet phase of CAS glass which is treated at 700 °C for 10 min by the elecric field ($E = 3$ kV/cm). It is observed that the electric field treatment promotes apparently the phase separation of the glass compared with the heat treatment of the glass in the absence of an electric field (Fig. 1). As shown in Fig. 2, the size of droplet phase in the vicinity of cathode is bigger than that of anode. The droplet phase near cathode are connected to each other, which indicates the higher growth of droplet phase. It is obvious that the electric field has made the size of droplet phase increase from anode to

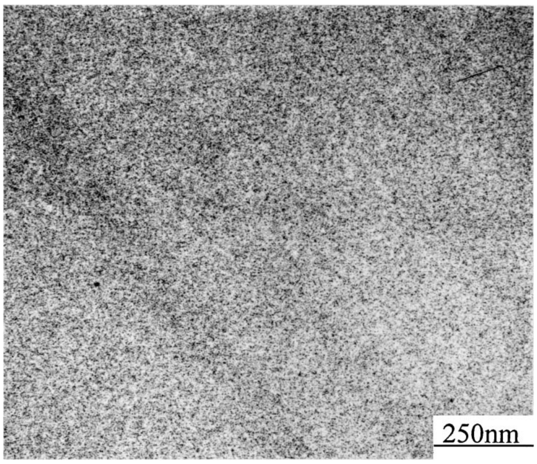


Figure 1 Morphology of phase separation of CAS glass at 700 °C for 10 min.

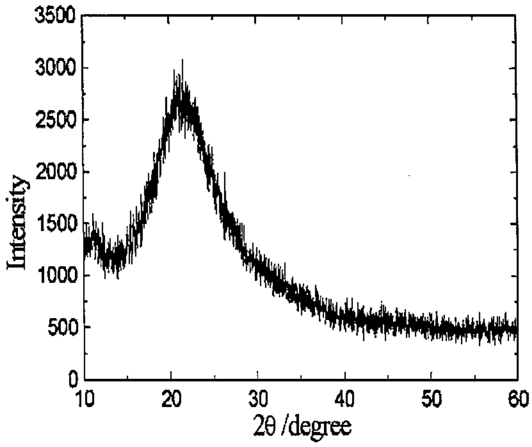


Figure 4 XRD patterns for CAS glass heat treated at 700 °C for 10 min ($E = 6$ kV/cm).

cathode. Therefore, we call the changing distribution of droplet phase ladder-shaped distribution. As shown in Fig. 3, increasing the electric field strength ($E = 6$ kV/cm) tends to increase the number of nucleation sites at the beginning of phase separation, but the increased size of particles is due to the growth of droplet phase to form the droplet phase interconnected with each other. This means that the electric field promotes greatly the phase separation of the glass. Fig. 4 shows that the interconnected microstructure is still amorphous. Fig. 5 demonstrates that the droplet phase is mainly rich in Ti^{4+} and Ca^{2+} compared with the matrix phase in the glass.

4. Discussion

4.1. The accelerating phase separation

The effect of an electric field can be understood in terms of a model of free energy difference. The initial energy

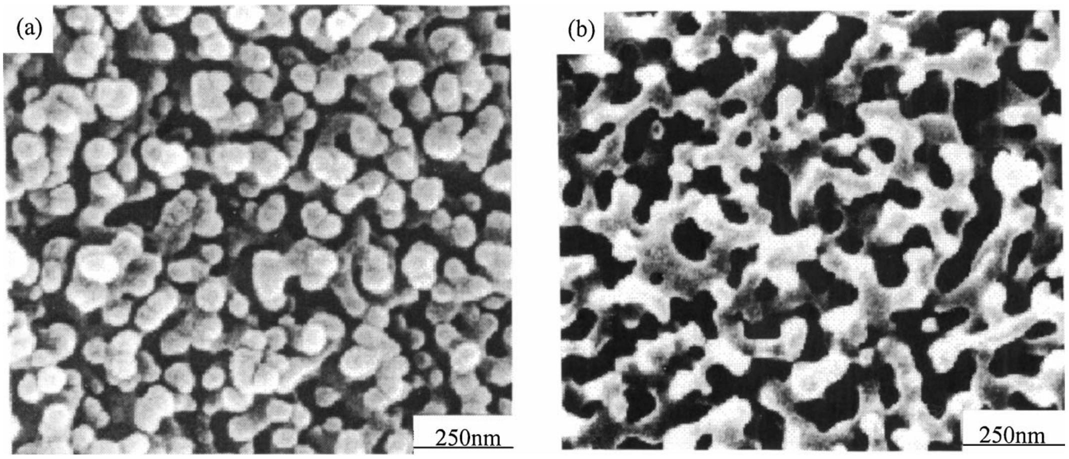


Figure 2 Morphology of phase separation of CAS glass at 700 °C for 10 min (3 kV/cm): (a) anode of the specimen and (b) cathode of the specimen.

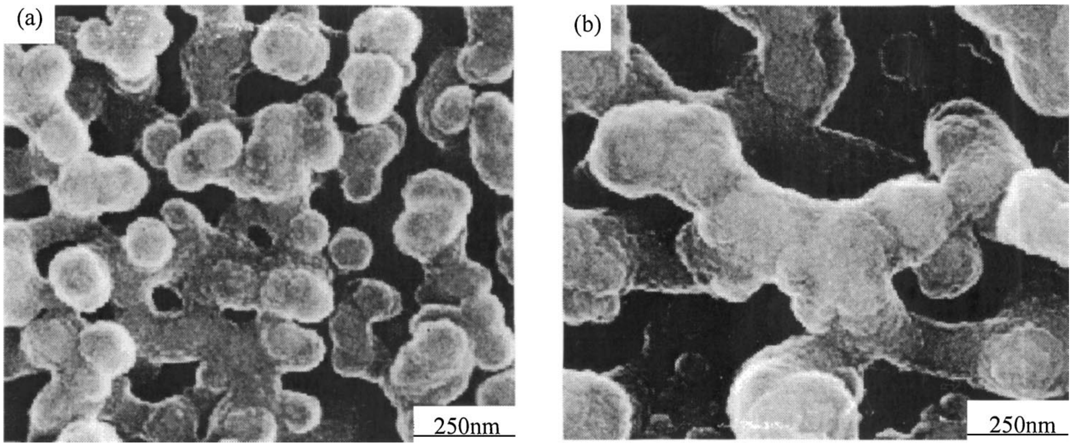
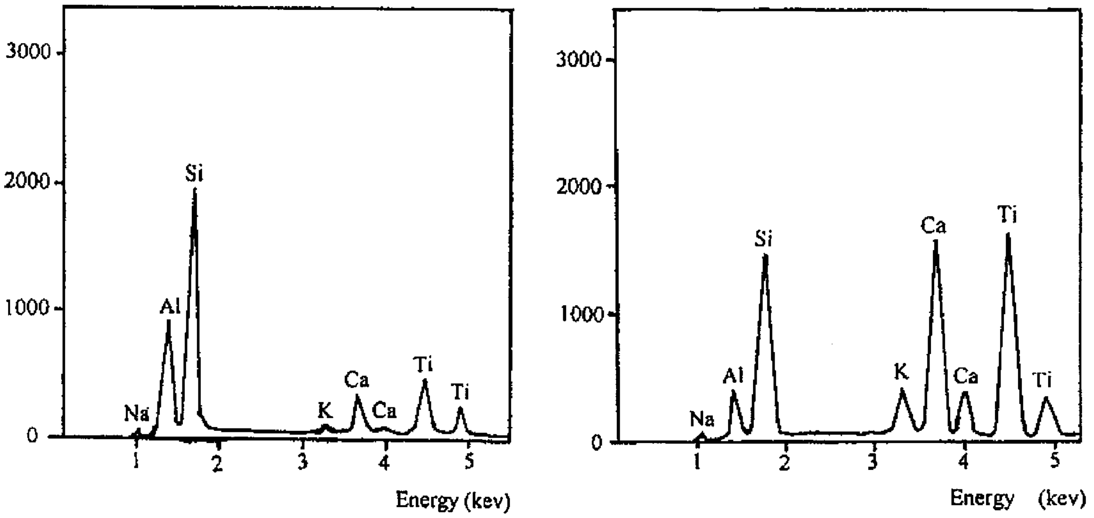


Figure 3 Morphology of phase separation of CAS glass at 700 °C for 10 min (6 kV/cm): (a) anode of the specimen and (b) cathode of the specimen.



(a) (b)

Figure 5 EDAX spectra of the matrix phase (a) and the droplet phase (b).

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

$$U_1 = \frac{1}{2}\int_V E_1 D_1 \, \mathrm{d}v \tag{1}$$

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, that of the medium exterior to it by V_2. The energy of the field owing to phase separation of glass is

$$U_2 = \frac{1}{2}\int_V ED \, \mathrm{d}v \tag{2}$$

and the change in energy resulting from phase separation [10]

$$U = U_2 - U_1 = \frac{1}{2}\int_{V_1} (ED_1 - E_1 D) \, \mathrm{d}v \tag{3}$$

Since $D_1 = \varepsilon_1 E_1$, $D = \varepsilon_2 E$ within V_1.

$$U = \frac{1}{2}\int_{V_1} (\varepsilon_1 - \varepsilon_2) E E_1 \, \mathrm{d}v \tag{4}$$

If at every point ε_2 is increased owing to phase separation of glass, the consequent variation in the electric energy will according to (4) be equal to

$$\delta U = -\frac{1}{2}\int \delta\varepsilon E E_1 \, \mathrm{d}v \approx -\frac{1}{2}\int \delta\varepsilon E^2 \, \mathrm{d}v \tag{5}$$

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

$$U \approx -\frac{1}{2}\iint_{\varepsilon_1}^{\varepsilon_2} E^2 \, \mathrm{d}\varepsilon \, \mathrm{d}v \tag{6}$$

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

$$\Delta G = \Delta G_0 + \Delta G_{\mathrm{E}} \tag{7}$$

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]

$$\Delta G_0 = \frac{4}{3}\pi\gamma^3 \Delta G_{\mathrm{v}} + 4\pi\gamma^2\sigma \tag{8}$$

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

$$\Delta G_E = -\frac{1}{2}\int_{V_1}\int_{\varepsilon_1}^{\varepsilon_2} E^2 \, \mathrm{d}\varepsilon \, \mathrm{d}v = -\frac{1}{2}E^2(\varepsilon_2 - \varepsilon_1)\frac{4}{3}\pi\gamma^3 \tag{9}$$

The change of free energy owing to the phase separation of glass in the presence of the electric field has the form shown in (10)

$$\Delta G = \frac{4}{3}\pi\gamma^3\left[\Delta G_{\mathrm{v}} - \frac{1}{2}E^2(\varepsilon_2 - \varepsilon_1)\right] + 4\pi\gamma^2\sigma \tag{10}$$

The variation of ΔG with γ is

$$\frac{\partial \Delta G}{\partial \gamma} = 4\pi\gamma^2\left[\Delta G_{\mathrm{v}} - \frac{1}{2}E^2(\varepsilon_2 - \varepsilon_1)\right] + 8\pi\gamma\sigma = 0 \tag{11}$$

The critical nucleus size is

$$\gamma_{\mathrm{c}} = \frac{2\sigma}{|\Delta G_{\mathrm{v}}| + \frac{1}{2}E^2(\varepsilon_2 - \varepsilon_1)} \tag{12}$$

TABLE I Dielectric constants of solid substances

Materials	TiO_2	CaO	CAS
Dielectric constants	85.8–170	10–12	5–9[12]

The free energy forming a critical nucleus size is

$$\Delta G_c = \frac{16\pi\sigma^3}{3\left[|\Delta G_v| + \frac{1}{2}E^2(\varepsilon_2 - \varepsilon_1)\right]^2} \tag{13}$$

As in the case of ionic crystals, the dielectric constants of inorganic glasses depend primarily upon the electronic and ionic polarization. Polarization of CAS glass containing TiO_2 nucleating agent is mainly determined by the electronic polarization of Ti^{4+} and the ionic conduction polarization of alkali. For the CAS glass system, owing to unstable TiO_4 groups in low temperature, TiO_6 groups are easy to form in the glass matrix. Then, the morphology of the Titanium-Calcium-rich particles is generated by a nucleation and growth mechanism. As shown in Table I, the dielectric constant of the droplet phase is larger than that of the glass matrix. Therefore, as shown in Equation 13, ΔG_c is reduced. This implies that the electric field promotes the phase separation of CAS glass. Furthermore, on increasing the electric field strength, ΔG_c is significantly decreased. This leads to the growth of droplet phase to form the interconnected microstructure owing to accelerating phase separation.

4.2. The ladder-shaped distribution

In an alkali silicate glass, the nonbridging oxygen ions and alkali ions become coulombically bonded together. The alkali ions are relatively easy to move through the rigid network under an electric field.

Consider ions of charge e which move parallel to the x-axis in a series of equal potential wells; see Fig. 6 (a). Let the well energy be G_0, assumed to be unaffected by the electric field. It is assumed that the ion makes attempts to jump from one well to the next with a frequency, γ. The probability of a successful jump in the positive x-direction, p^+, and that of the negative x-direction, p^-, have the same value [9].

$$p^+ = p^- = \gamma \exp\left(-\frac{G_0}{kT}\right) \tag{14}$$

where T is temperature; k is Baltzman constant.

Now consider the effect of adding an electric field in the $+x$-direction having a local value, E. The electric field in effect shifts the energy levels, Fig. 6(b), and the forward jump probabilities now become bigger than that of backward jump.

$$p^+ = \gamma \exp\left[-\left(G_0 - \frac{1}{2}\ell E\lambda\right)\Big/kT\right] \tag{15}$$

λ is the distance between two potential well.

Therefore, it is obvious that the resulting increase in mobility will occur only in the direction of the electric field.

The force on every ions of the glass applying an electric field is

$$F = \ell E \tag{16}$$

A mean drift velocity owing to electric field force

$$v = BF \tag{17}$$

where B is migration rate of ions.

$$B = \frac{D}{kT} \tag{18}$$

where D is diffusion coefficient.

The diffusion mass of ions by electric field

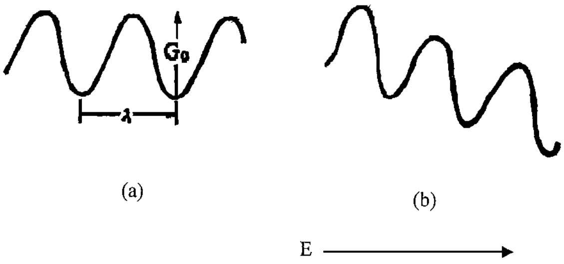
$$J = cv = BFc = \frac{D}{kT}Fc \tag{19}$$

If the contents of ions in the glass system are uniformly distributed before heat treatment and D is a constant, we can get the changing rate of ion concentration at every point.

$$\frac{\partial c}{\partial t} = -D\frac{\ell E}{kT}\frac{\partial c}{\partial x} \tag{20}$$

Seeing also Ref. [13] and solving Equation 20, we have the distribution of ion concentration at the same time and temperature but different electric field strengths. Fig. 7 shows the increase in the ionic concentration from the anode to the cathode of the specimen, and for $E = 6$ kV/cm, the increase in the ionic concentration is greater than that of $E = 3$ kV/cm.

Owing to the greater concentration of mobile ions is greater at cathode than at anode, the driving force



(a) (b)

Figure 6 Representation of potential wells: (a) in the absence of an electric field and (b) in the presence of an electric field.

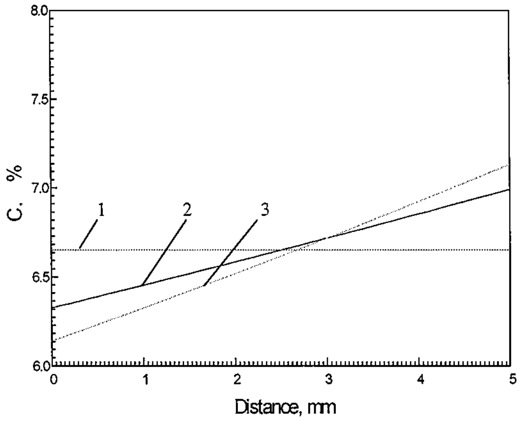


Figure 7 Distribution of ions concentration from the anode to the cathode 1 initial concentration; 2: $E = 3$ kV/cm; 3: $E = 6$ kV/cm.

of nucleation of phase separation increases with the ion concentration from cathode to anode. The greater driving force of nucleation means that phase separation can take place easily near cathode than near anode. In addition the higher concentration of mobile ions at cathode will reduce the viscosity of the glass, and then facilitate the diffusion of these ions. This leads to the increase in the growth speed of droplet phase. With increasing the electric field strength ($E = 6$ kV/cm), the difference of mobile ions concentration between anode and cathode is more significant. Therefore, the ladder-shaped distribution is more obvious than that of $E = 3$ kV/cm.

5. Conclusions

Owing to the electronic and ionic conduction polarization in the CAS glass, the accelerating phase separation and ladder-shaped distribution of the droplet phase are induced in the presence of the electric field. And, increasing the electric field strength to 6 kV/cm, the effect of the electric field is more significant than that of $E = 3$ kV/cm.

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