

## NON-ISOTHERMAL DEVITRIFICATION AND ELECTRICAL CONDUCTIVITY OF GLASSES NEAR THE $\text{Li}_2\text{SiO}_3$ COMPOSITION

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### ABSTRACT

The devitrification behaviour and the electrical conductivity of five glasses near the lithium metasilicate composition have been studied using differential thermal analysis, X-ray diffraction and impedance analysis. All the studied glasses devitrify in two steps. The influences of replacing  $\text{SiO}_2$  by  $\text{Al}_2\text{O}_3$  and of the  $\text{LiO}_2$  content on the activation energy of crystal growth and of electrical conductivity have been pointed out.

### INTRODUCTION

Vitreous electrolytes are increasingly being used in electrochemical sensors, batteries and electrochromic devices. Glasses have many advantages over crystalline electrolytes because of their physical isotropy, the absence of grain boundaries, their continuously variable composition and their good workability.

In previous papers [1,2] the effect of the substitution in a base glass of composition  $\text{AgPO}_3$  of a small amount of  $\text{P}_2\text{O}_5$  with different  $\text{M}_2\text{O}_3$  oxides was reported. In this way, it was possible to improve the electrical conductivity and thermal stability of the glass.

The aim of the present work was to evaluate the effect on the devitrification behaviour and the electrical conductivity of: (a) replacing  $\text{SiO}_2$  by small amounts of  $\text{Al}_2\text{O}_3$  in an  $\text{Li}_2\text{SiO}_3$  glass; and (b) increasing the amount of  $\text{Li}_2\text{O}$  in an  $\text{Li}_2\text{O} \cdot 0.05\text{Al}_2\text{O}_3 \cdot 0.9\text{SiO}_2$  glass.

### EXPERIMENTAL

Two series of glasses, whose composition are expressed by the following formulae, were prepared: (I)  $\text{Li}_2\text{O} \cdot x\text{Al}_2\text{O}_3 \cdot (1 - 2x)\text{SiO}_2$  with  $x = 0.00, 0.05$  and  $0.10$ ; and (II)  $(1 + y)\text{Li}_2\text{O} \cdot 0.05\text{Al}_2\text{O}_3 \cdot 0.9\text{SiO}_2$  with  $y = 0.00, 0.05$  and  $0.15$ .

The glasses were obtained by melting pure reagents in a platinum crucible in an electric oven. The melts were quenched by casting them between two brass plates.

Differential thermal analysis (DTA) curves of  $\approx 50$  mg bulk samples at different heating rates ( $5\text{--}20^\circ\text{C min}^{-1}$ ) were recorded in air. Powdered  $\text{Al}_2\text{O}_3$  was added to improve the heat transfer between bulk samples and the sample holder of the DTA apparatus. A Netzsch thermoanalyser (Model 404M) was used, and powdered  $\text{Al}_2\text{O}_3$  was the reference material. The phases crystallizing during the DTA runs were identified by X-ray diffraction (XRD). A Guinier de Wolfe camera and Cu  $K\alpha$  radiation were used.

The electrical conductivity measurements were carried out in the temperature range  $25\text{--}80^\circ\text{C}$ , keeping the samples in a dry condition. The electrical conductivities were determined using a Solartron 1250 frequency response analyser and a Solartron 1286 electrochemical interface, both controlled by a Hewlett–Packard 86-B desktop computer. Gold electrodes were made on the specimen faces by vacuum sputtering.

## RESULTS AND DISCUSSION

Figure 1 shows the DTA curves of the glasses of series I recorded in air at  $10^\circ\text{C min}^{-1}$ . All curves exhibit a slope change at  $425^\circ\text{C}$  followed by two exothermic peaks, the first one at  $475^\circ\text{C}$  and the second ranging between  $581$  and  $672^\circ\text{C}$ . The slope change is due to the glass transition. The XRD analyses have shown that in all the glasses of the series, the first exothermic peak can be attributed to the growth of  $\text{Li}_4\text{SiO}_4$  crystals while the second exothermic peak is due to their conversion in  $\text{Li}_2\text{SiO}_3$  crystals. The glass transition temperature and the devitrification mechanism of  $\text{Li}_2\text{SiO}_3$  glass [3] are therefore not affected by the substitution of  $\text{SiO}_2$  by  $\text{Al}_2\text{O}_3$ . The greater the replacement of  $\text{SiO}_2$  by  $\text{Al}_2\text{O}_3$ , the higher the temperature of the second crystallization peak. This shift towards higher temperatures can be attributed to the presence of  $\text{Al}_2\text{O}_3$  making the conversion of  $\text{Li}_4\text{SiO}_4$  crystals into  $\text{Li}_2\text{SiO}_3$  crystals more difficult.

The devitrification behaviour of glasses of series II is quite similar to that of the glasses of series I, see Fig. 2. The glass transition temperature ( $425^\circ\text{C}$ ) and the two-step devitrification mechanism are not affected by an increase in  $\text{Li}_2\text{O}$ . The increase in  $\text{Li}^+$  ions increases the number of nuclei of  $\text{Li}_4\text{SiO}_4$  crystals so that the first crystallization peak is shifted towards lower temperatures.

The two crystallization steps in the studied glasses can be described by the following equation [4]

$$-\ln(1 - \alpha) = (A/\beta^n) \exp(-nE/RT) \quad (1)$$

where  $\alpha$  is the volume fraction crystallized at the temperature  $T$ ,  $\beta$  the DTA

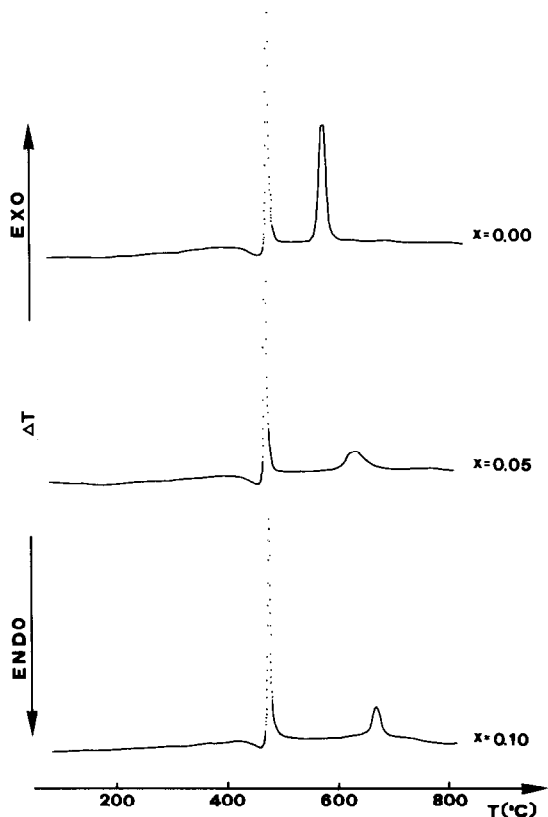


Fig. 1. DTA curves of series I glasses at  $10^{\circ}\text{C min}^{-1}$ .

heating rate,  $E$  the activation energy for the crystal growth and  $A$  a constant. The morphological index  $n$  is related to the crystal shape (for three-dimensional crystals,  $n = 3$ ; plate-like crystals,  $n = 2$ ; rod-like crystals,  $n = 1$ ). The higher the value of  $n$ , the sharper the DTA crystallization peak [5]. In all DTA curves of the studied glasses, the first crystallization peak is notably sharper than the second. This behaviour is consistent with the crystallization mechanism suggested by XRD analysis. The first crystallization peak is due to the growth of granular ( $n = 3$ )  $\text{Li}_4\text{SiO}_4$  crystals, the second is due to the growth of acicular ( $n = 1$ )  $\text{Li}_2\text{SiO}_3$  crystals.

Assuming that at the peak temperature,  $T_p$ , the degree of crystallization  $\alpha$  reaches the same specific value and is not dependent on the heating rate  $\beta$ , the activation energy  $E$  for the crystal growth can be evaluated from the DTA curves by the following equation [6]

$$\ln\beta = -(E/R)(1/T_p) + \text{const.} \quad (2)$$

Multiple DTA runs were performed at different heating rates,  $\beta$ , and  $\ln\beta$  versus  $1/T_p$  was plotted. A straight line was obtained in all cases for each of

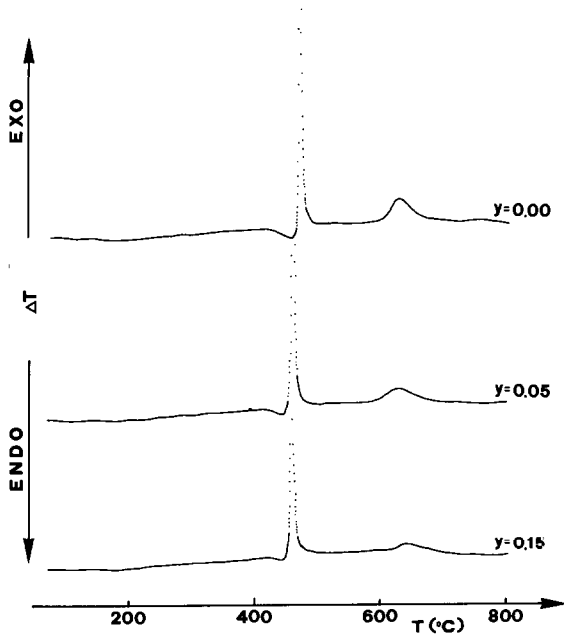


Fig. 2. DTA curves of series II glasses at  $10^{\circ}\text{C min}^{-1}$ .

the two crystallization peaks. The values of  $E$  calculated from their slopes are plotted in Figs. 3 and 4 as a function of glass composition.

As can be observed in Fig. 3, the activation energy for  $\text{Li}_4\text{SiO}_4$  crystal growth is little affected by the replacement of  $\text{SiO}_2$  by  $\text{Al}_2\text{O}_3$ , while the activation energy for the  $\text{Li}_2\text{SiO}_3$  crystal growth is notably increased by the presence of  $\text{Al}_2\text{O}_3$ . The substitution of  $\text{SiO}_2$  by  $\text{Al}_2\text{O}_3$  should not appreciably change the number of  $\text{SiO}_4$  units in the glass structure but the presence of  $\text{Al}^{3+}$  ions makes their polymerization more difficult. In the glasses of series II, the increase in  $\text{Li}_2\text{O}$  content increases the number of  $\text{SiO}_4$  units, as demonstrated by the shift towards lower temperatures of the first crystalliza-

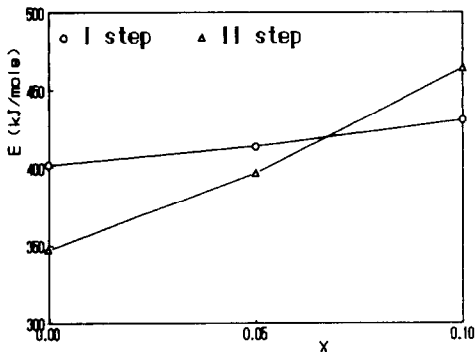


Fig. 3. Activation energy of crystal growth of series I glasses.

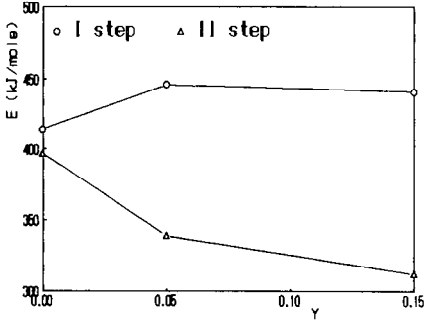


Fig. 4. Activation energy of crystal growth of series II glasses.

tion peak, Fig. 2, and enhances their polymerization, as suggested by the decrease of the activation energy for the second crystallization step, see Fig. 4.

The complex impedance measured in the frequency range 60–0.5 kHz allowed us to obtain the glass bulk d.c. conductivity  $\sigma$  by means of the usual impedance analysis [7,8]. The values of  $\sigma$  at 25 °C range between  $2.5 \times 10^{-7}$  and  $7.1 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ . It is known [9] that the dependence of the electrical conductivity  $\sigma$  on the temperature can be expressed as

$$\sigma = \sigma_0 \exp(-E_\sigma/RT) \quad (3)$$

where  $\sigma_0$  is a constant whose value depends on the vibration frequency and the jump distance.  $E_\sigma$  is the electrical conduction activation energy, i.e. the average value of the potential barrier heights that  $\text{Li}^+$  ions must overcome in their jumps. By plotting  $\ln\sigma$  against  $1/T$ , straight lines were obtained for all the glass studied. The values of the electrical conduction activation energy  $E_\sigma$  calculated from the slopes of the straight lines are plotted in Fig. 5 as a function of the glass composition. The greater the level of  $\text{SiO}_2$  replaced by  $\text{Al}_2\text{O}_3$  or the higher the number of  $\text{Li}^+$  ions, the lower the  $E_\sigma$  value. This behaviour can be attributed to a change in the glass structure. In the glasses of series I, the replacement of  $\text{SiO}_2$  involves a change in the coordination of

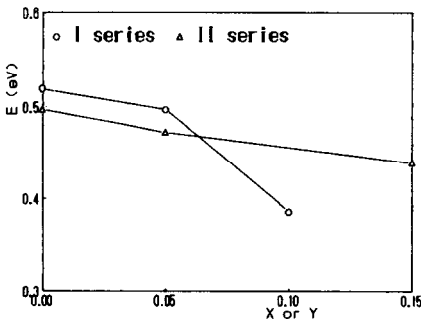


Fig. 5. Activation energy of electrical conductivity.

the  $\text{Li}^+$  ions; in the glasses of series II, an increase in  $\text{Li}_2\text{O}$  content leads to a more fragmented structure.

## CONCLUSIONS

From the experimental results the following conclusions can be drawn.

1. All the studied glasses devitrify in two steps, i.e. at temperatures just above the glass transition temperature,  $\text{Li}_4\text{SiO}_4$  crystals are formed which are converted at higher temperatures into  $\text{Li}_2\text{SiO}_3$  crystals.

2. Replacing  $\text{SiO}_2$  by  $\text{Al}_2\text{O}_3$  leads to an increase in the activation energy for the second crystallization step and to a decrease in the activation energy of electrical conductivity.

3. An increase in  $\text{Li}_2\text{O}$  content leads to a decrease in the activation energy of the second crystallization step and of electrical conductivity.

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