DEVITRIFICATION OF ALUMINOSILICATE GLASSES UNDER APPLIED ELECTRIC FIELDS

I. THE SYSTEM $Al_2O_3 \cdot 2SiO_2$

K. J. D. MacKenzie and I. W. M. Brown*

Chemistry Division, Department of Scientific and Industrial Research, Private Bag, Petone;
*Chemistry Department, Victoria University of Wellington, Wellington, New Zealand

Electric fields have been shown by a combined DTA-electrolysis technique to decrease the temperature of the exothermic devitrification of aluminosilicate glasses derived from kaolinite by up to 30°. A layer of extremely crystalline alkali aluminium silicate is formed at the cathode as a result of migration of alkali metal ions to that electrode; underlying this is a region containing mullite and a high concentration of bubble-like voids. The distribution of Al and Si is unchanged by electrolysis. These results are interpreted in terms of an electrolysis mechanism involving co-operative migration of alkali metal ions and protons to the cathode. An observed lowering of the heat of devitrification by the electric field is ascribed to a decrease in entropy of the electrolysed system.

The advent of glass-ceramics has led to considerable interest in nucleation and phase separation phenomena in many glassy solids, including the binary system $Al_2O_3 - SiO_2$ [1]. Since a knowledge of the factors which control the devitrification process is of both practical and theoretical importance, much recent research has been directed toward systems which display metastable liquid immiscibility; such systems include $Al_2O_3 - SiO_2$.

As phase separation in another glass-forming system $(CaO - Al_2O_3 - SiO_2 - MgO)$ has been found to be influenced by applied DC electric fields [2] and such fields are also known to assist formation of mullite and cristobalite in crystalline aluminosilicates [3], the present study was undertaken to determine whether devitrification of an aluminosilicate glass can be controlled by solid state electrolysis.

The glass used in this study was made from dehydroxylated kaolinite, and has the composition 46.26 wt. % Al_2O_3 (33.56 mol % Al_2O_3), 48.00 wt. % SiO_2. This composition falls within the range of metastable liquid immiscibility of the system [1] and corresponds to a composition which separates apparently by a spinodal mechanism rather than the classical mechanisms of nucleation and growth [1].

The chief experimental technique used in this study was DTA which gave both a measurement of the devitrification temperature under various electrolysis conditions and an estimate of the heat evolved in the devitrification reaction. The reactant and product phases were investigated by X-ray diffractometry, i.r. spectrophotometry and electron microprobe analysis.

Experimental

Sample preparation

Preparation of the kaolinite glass has been described in detail elsewhere [4]. Typical analyses of the original kaolinite and the resulting glass are given in Table 1. The fused samples were translucent and amorphous to X-rays. Parallel-faced pellets about 3 mm thick were ground from small globules of the glass (~ 0.2 g). A thin platinum film was then vacuum-deposited on to the flat electrode faces of the weighed pellet. The thickness of the pellets was accurately determined by micrometer.

Table 1

Typical analyses of dehydroxylated kaolinite (13.75% ignition loss) starting material and the resulting glass. Major constituent analyses by atomic absorption, trace element analyses by semi-quantitative D.C. arc spectroscopy

Constituent	Kaolinite	Glass	Constituent	Kaolinite	Glass
	%	%		%	%
SiO_2	49.39	48.96	Al_2O_3	47.88	47.96
Fe_2O_3	0.50	0.52	TiO_2	0.02	0.02
MgO	0.14	0.18	CaO	0.10	0.10
Na_2O	0.13	0.18	K_2O	0.81	0.83
	ppm	*ppm*		*ppm*	*ppm*
Ba	—	500	Zr	100	100
B	50	50	Mn	25	25
Ga	25	25	Sn	25	10
Cr	10	10	Zn	10	10
Cu	25	10	Ni	—	10
Pb	10	5	V	5	5
Be	10	5	Ag	—	0.1

DTA electrolysis technique

The specially fabricated cell for simultaneous DTA and electrolysis has been described elsewhere [5]. All the thermal analyses were performed in a Deltatherm thermal analyser under ambient atmosphere at a heating rate of $10°/min$.

Temperature calibration was carried out using analytical grade $BaCO_3$ which undergoes an endothermic transition at 819°. Correlation of the measured DTA peak areas with the heat of reaction was carried out using pure kaolinite powder for which a value of 9 kcal/mol was assumed for the exothermic reaction at 980° [7].

At a preselected electrolysing temperature (in most cases 25°) a voltage was applied to the electrodes from a Philips PW4022 high voltage power supply. Voltages greater than 1.2 kV had to be applied gradually to prevent arcing at

lower temperatures. After reaction, the onset and peak temperatures were read off and the areas under the peaks measured by planimeter. Reproducibility of the peak temperature measurements was about 0.5% ($\pm 2°$) but because the method of measuring the onset temperatures was sensitive to peak shape, these measurements varied up to 3% ($\pm 12°$). The errors in reproducibility increased with decreasing voltage, being greatest at 0 kV. The reproducibility of the peak areas, after correction for sample weight, varied from 20% below 0.5 kV to 3% at 1.2 kV; these large errors are due to differences in peak shape and the difficulty of estimating the position of the baseline.*

Examination of the electrolysed product

After devitrification, both faces of each pellet were examined in a Philips PW4210 diffractometer using Ni-filtered CuK_α radiation. Thin, freshly prepared disc-shaped samples were examined in a Perkin-Elmer 21 i.r. spectrophotometer, particular attention being paid to the hydroxyl stretching region ($3000 - 4000 \text{cm}^{-1}$). After electrolysis, the platinum film was polished off and the i.r. spectrum determined again. In some cases, electrolysed and unelectrolysed devitrified disc-shaped samples were sectioned perpendicular to their faces, set in Araldite, polished and examined by optical microscopy in reflected light and by an A. E. I. electron microprobe analyser. The same polished samples were also examined by scanning electron microscopy (SEM).

Results

(a) Effect of electrolysis on devitrification

In the following, the temperature parameter measured by DTA is termed the devitrification temperature. This is the temperature of the maximum of the exothermic DTA peak, and is therefore not necessarily the maximum devitrification temperature, which also depends on other factors (e.g. heating rate, etc.).

The variation in devitrification temperature with applied voltage is shown in Fig. 1, from which it is seen that in all cases devitrification is enhanced by the application of an electric field; at the highest field strength used here (5×10^5 V/m) the reaction temperature was lowered by 30°.

X-ray examination showed that in all samples which had been electrolysed at the devitrification temperature for several hours, a well crystallized alkali aluminium silicate with an X-ray pattern resembling synthetic kalsilite ($KAlSiO_4$)

---

* Other methods of measuring DTA peak areas are available which are said to give results less sensitive to peak shape (see, for example "DTA", Pt. 1, Ed. R. C. MacKenzie, Academic Press, p. 51). The simpler method was used here, however, since because of the baseline drift introduced by the design of the apparatus and other experimental uncertainties a more elaborate method is not justified.

(ASTM Card No. 11 – 579) was the sole phase detectable by X-rays at the negative electrode surface. However, when this surface layer was polished off, the region immediately underlying exhibited an X-ray pattern corresponding to fairly well crystallized mullite. By contrast, only a small amount of poorly crystalline mullite and a cristobalite pattern of approximately similar intensity was found in the
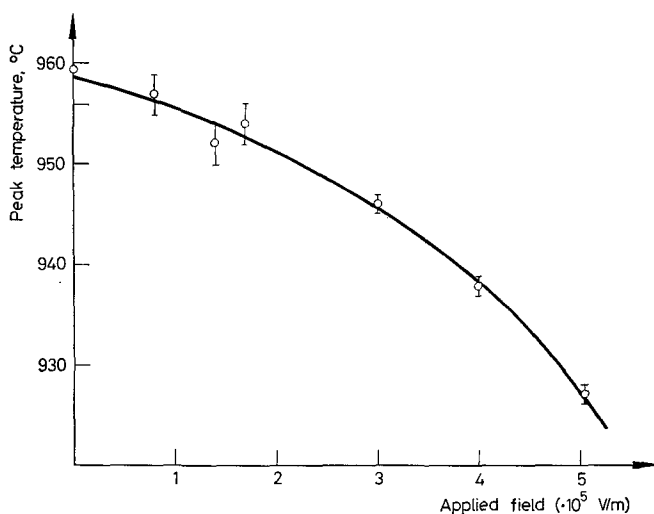

Fig. 1. Variation of DTA devitrification peak temperature with applied electric field. Heating rate: 10°/min. Ambient atmosphere

region of the positive electrode. The textural differences at the two electrode faces were quite apparent in reflected light under a low power microscope objective (Fig. 2), being most marked at higher field strengths and long electrolysis times. Similar differences in crystalline texture at the cathode and anode faces have been reported in electrolysed kaolinite [3] and MgO pellets [8] although unlike the present case these differences were not visually apparent.

In pellets sectioned perpendicular to their faces for electron microprobe examination a distinct band could be distinguished extending 0.25 mm inwards from the negative electrode surface. Examination of this band by electron microprobe analyser revealed the presence of numerous spots of about 10 μm dia. in this region. These spots were almost entirely depleted of Al, Si, alkali and alkaline earth metals, and were therefore identified as bubbles. This was confirmed by SEM (Fig. 3). The material at the positive electrode was virtually free of bubbles; by contrast, unelectrolysed devitrified samples contained a number of very small bubbles distributed throughout the sample.

An apparent increase in the Si and Al content at the cathode face and a corresponding decrease at the anode face is probably not real, being almost certainly
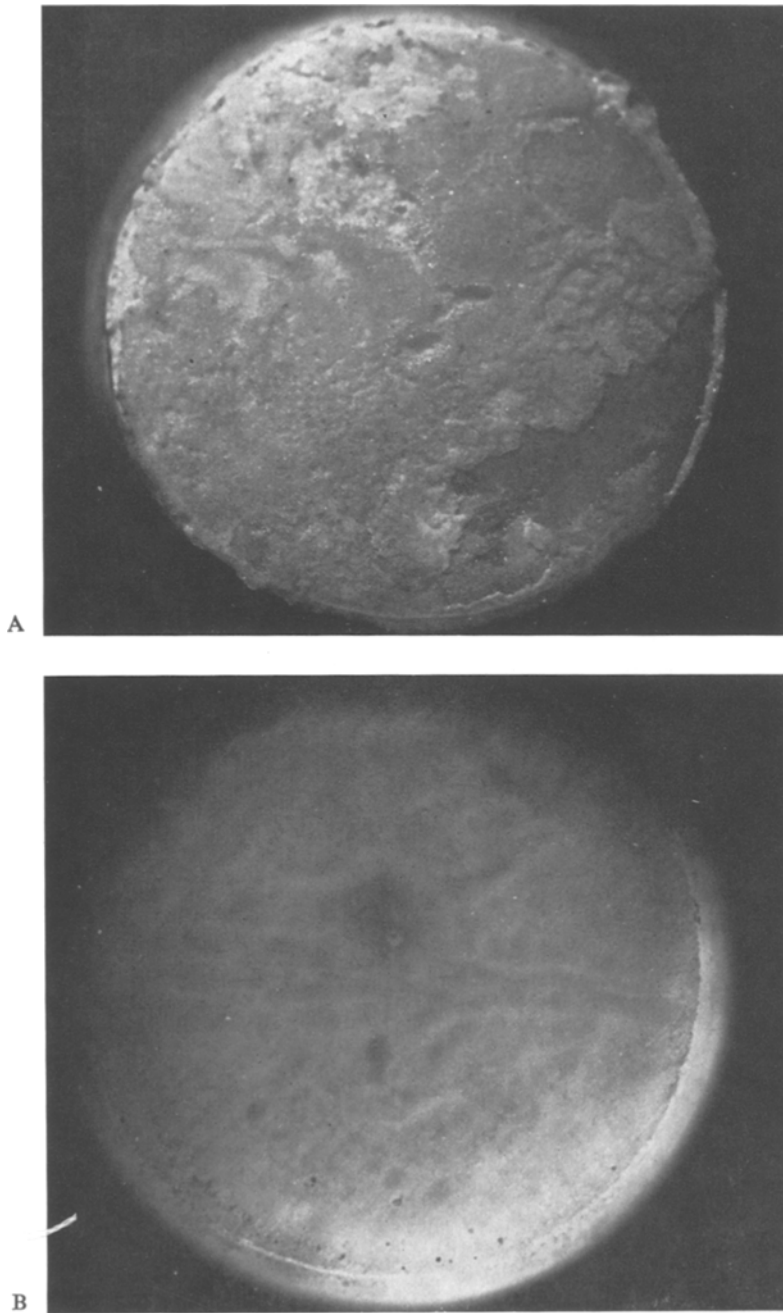
Fig. 2. Micrograph of aluminosilicate glass pellet after electrolysis for 6 h at 1000°. Magnification: 20×. A. Cathode face. B. Anode face
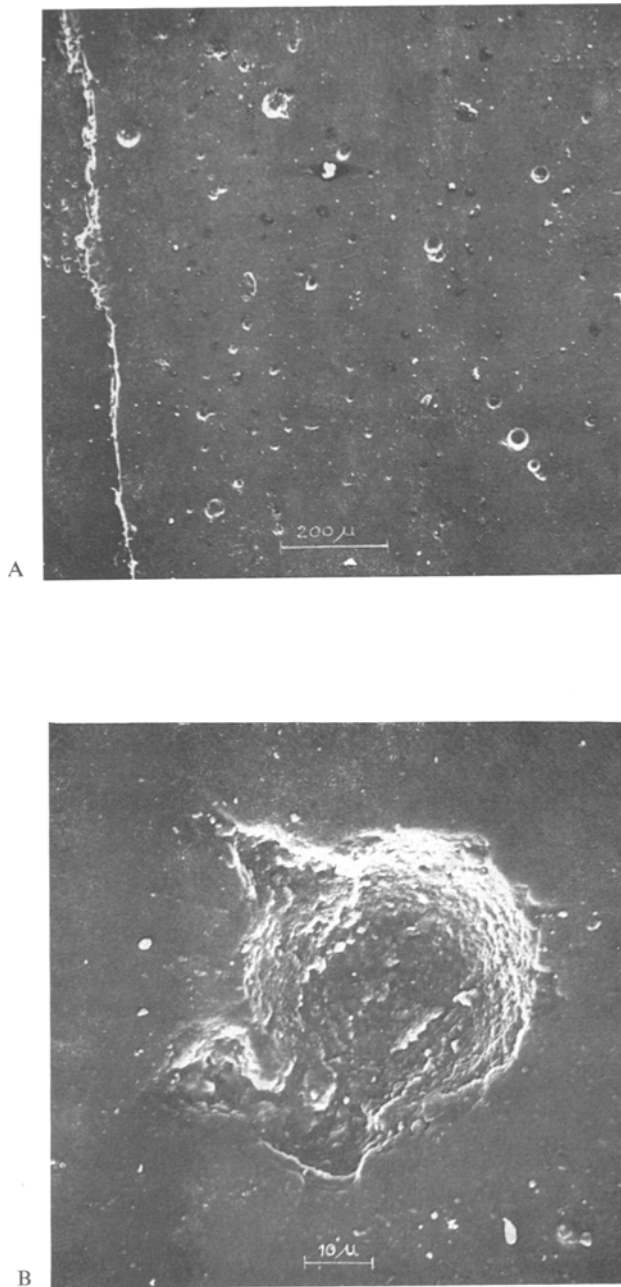
Fig. 3. Scanning electron micrographs of the cathode region of aluminosilicate glass electrolysed for 6 h at 1000°C. A. General view, showing cathodic bubble crater. B. Close-up view of bubble crater

caused by topographical factors introduced by the polishing technique since an identical effect was observed in the unelectrolysed control samples in which no preferential migration should have occurred but which had been mounted and polished in an identical manner.

I.r. transmission spectroscopy of unreacted disc-shaped specimens showed an appreciable, broad absorption band at $3550\ cm^{-1}$ (2.82 μm). On devitrification, this band retained its intensity but became much sharper and shifted to $3670\ cm^{-1}$ (2.73 μm), in good agreement with the spectral position reported for the $Si-OH$ groups in fused silica in which the hydroxyls had been incorporated during a flame fusion process [9]. Similar results were recorded for the electrolysed samples.

(b) Effect of temperature of voltage application (tva) on devitrification

Although in most of the experiments the electrolysing voltage was applied at room temperature and continued throughout the heating cycle, in those experiments in which tva was sufficiently high for appreciable current (0.5 mA) to be
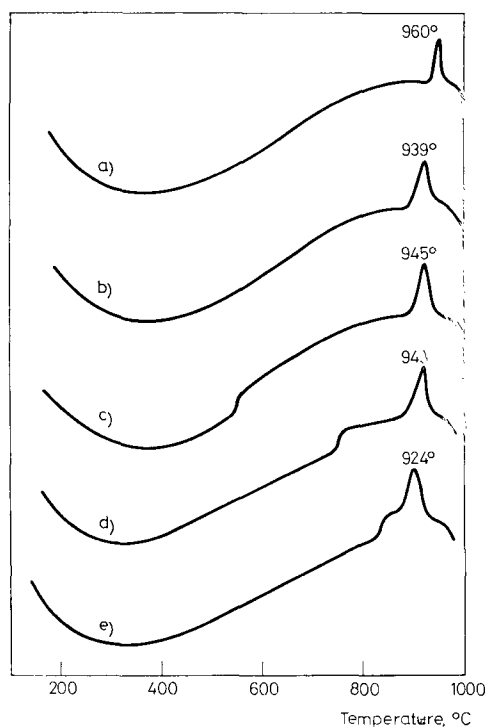

Fig. 4. Typical DTA traces of aluminosilicate glasses in which an electric field (4.0×10^5 V/m) was applied at various temperatures. (a) Sample unelectrolysed. (b) Field applied at 20°. (c) 550°. (d) 750°. (e) 830°

carried (430°), the voltage application was accompanied by a momentary steepening of the baseline slope (Fig. 4), suggestive of localized electrical heating in the sample cell. The effect is probably not due to electrical interference acting on the thermocouples, as it was not observed in experiments where the voltage was applied during heating from room temperature; moreover, the baseline was unaffected by switching the field off and on once electrical and thermal conditions had stabilized.
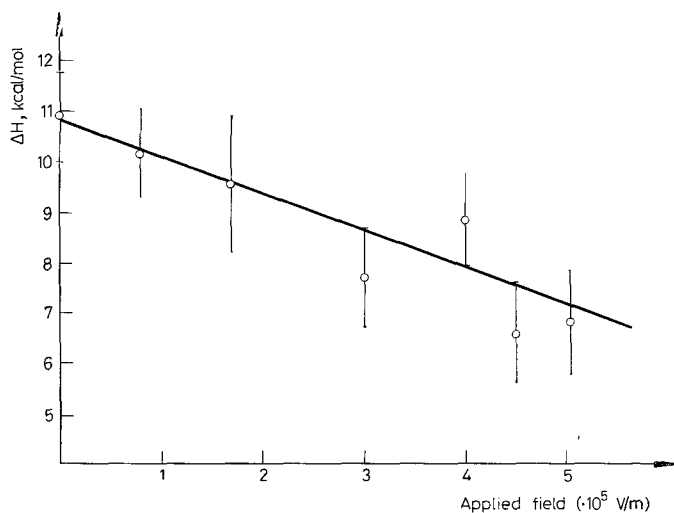

Fig. 5. Variation of heat-of-reaction with applied electric field

In all cases the baseline recovered its original slope in about 3 min., the peak temperature being unchanged by this phenomenon except where tva was very close to the exotherm (Fig. 4e). In the latter case there was apparently insufficient time for thermal balance to be restored, the local temperature rise in the sample being sufficient to initiate devitrification. In several runs the magnitude of the electrical heating was investigated by placing an independent thermocouple in contact with the upper electrode but insulated from it by a thinly ground vitreous silica plate. By this means, local temperature rises of up to about 1.5° were recorded after voltage application, the maximum being reached 3 – 5 min. after the start of electrolysis. No such temperature rises were recorded in samples electrolysed from room temperature.

(c) Effect of applied voltage on devitrification peak area

The areas under the devitrification peaks, which are related to the amount of heat liberated in the reaction, were found to *decrease* as the applied voltage was increased (Fig. 5). Although these measurements are subject to considerable

experimental error, it is clear from Fig. 5, in which the areas have been expressed as heats of reaction, that this effect is outside the experimental error. This trend is in the opposite sense to experiments in which the devitrification temperature is lowered by the addition of transition metal ions [10]; in these cases decreased peak temperatures are usually accompanied by *increased* peak areas.

Discussion

The stable composition ranges of binary silicate glasses are controlled by the amount of the second oxide which can enter the silicate network. In the $Al_2O_3 - SiO_2$ system, only a small amount (between $5 - 10$ mole %) of alumina can enter the system by replacement of tetrahedral Si with Al^{IV} since to maintain charge balance, one oxygen ion must tribridge three tetrahedra for every one aluminium-for-silicon replacement [1]. This process results in a dense, high-energy system which favours a two-phase assemblage. At higher alumina concentrations, corresponding to the composition region of the present study, the excess alumina may occur in a randomized octahedral network, modified by AlO_4 and SiO_4 tetrahedra [1]. Thus, the octahedral regions will ultimately give rise to mullite, itself containing octahedral AlO_6 columns cross-linked by tetrahedral AlO_4 and SiO_4 [11] while the highly siliceous regions will form cristobalite on devitrification. There is evidence to suggest that the mechanism by which this highly metastable system separates into two phases involves a spinodal process [1, 12]. In the preparation of the present glasses, very short times (of the order of a second) elapsed between melting and supercooling; although these cooling rates are too fast to allow the development of a coarse two-phase structure, the material on which the present devitrification studies were made may have inherited some elements of phase separation by virtue of its preparation.

Since the spinodal region is traversed during quenching, such spinodal phase separation as may occur at that stage will not be acted upon by the external field, which is only applied during reheating. If, during the electrolysis, further spinodal processes should occur, a recent theoretical treatment of this situation [13] suggests that electric fields of the strength used here should slightly inhibit spinodal decomposition under the present reaction conditions. Again, a theoretical treatment of the effect of electric fields on nucleation [14] has shown the rate of this process to be independent of the field where the dielectric constant of the final phase is similar to that of the initial phase, as is probably the case here (see p. 618). Hence, the effects observed here are probably due to the DC conductance of the system, which is not taken into account in either of the above theoretical treatments.
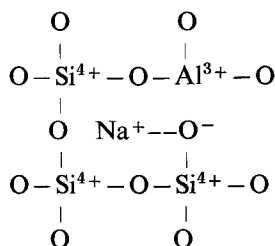
The effect of electric fields on conducting systems arises from the transport of mobile, charged species to one or other electrode or both. If the species is a nucleating agent, its effect will be most apparent at the electrode region in which

it accumulates. A similar result would be expected if some network-forming species was transferred; transport of Si and/or Al to the cathode, however, appears unlikely from the electron microprobe results.
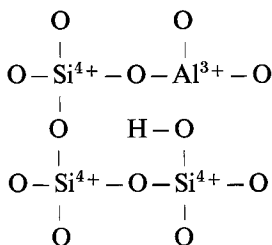
The most significant charge carriers are apparently the alkali metal ions since on prolonged electrolysis these accumulate at the cathode in sufficient concentration to form a coherent layer of alkali aluminium silicate which in the present potassium-rich samples tends towards the kalsilite composition (glasses derived from kaolinite containing more sodium than potassium should form compounds of the nepheline type). Another possible charge carrier which is also a nucleating agent [3] is the proton, the presence of which is confirmed by i.r. spectroscopy.

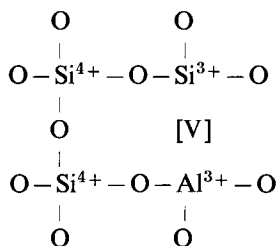### The role of alkali ions and protons in the electrolysis process

The alkali ions in aluminosilicate glasses probably occur in interstitial sites and are associated with a network substituent of lower valency than Si^{4+} (e.g. Al^{3+}), since on X-irradiation the glasses turn brownish-yellow. The centre responsible for irradiation colour has been said to be [9]

$$
\begin{array}{ccc}
& O & & O \\
& | & & | \\
O- & Si^{4+} & -O- & Al^{3+} & -O \\
& | & & \\
& O & & Na^{+}--O^{-} \\
& | & & | \\
O- & Si^{4+} & -O- & Si^{4+} & -O \\
& | & & | \\
& O & & O
\end{array}
$$

On electrolysis, the alkali ions proceed to the cathode, being progressively replaced by protons to form

$$
\begin{array}{ccc}
& O & & O \\
& | & & | \\
O- & Si^{4+} & -O- & Al^{3+} & -O \\
& | & & \\
& O & & H-O \\
& | & & | \\
O- & Si^{4+} & -O- & Si^{4+} & -O \\
& | & & | \\
& O & & O
\end{array}
$$

The hydroxyl group thus formed is said to be particularly stable [9] and is responsible for the observed i.r. band at about 2.7 μm. The present glasses also fluoresce under uv irradiation; according to Hetherington et al. [9] this is due to the presence of a centre such as

$$
\begin{array}{ccc}
& O & O \\
& | & | \\
O- & Si^{4+}-O-Si^{3+}-O \\
& | & \\
& O & [V] \\
& | & \\
O- & Si^{4+}-O-Al^{3+}-O \\
& | & | \\
& O & O
\end{array}
$$

where V is a vacancy, and Si^{3+} is a reduced species occurring in conjunction with a network substituent (in this case Al). On electrolysis the vacancies also move to the cathode, the reduced species becoming Si^{4+} [9]. Thus the electrolysis mechanism envisaged involves the movement of vacancies, alkali ions and protons, to the cathode. The proposed electrolysis mechanism is shown schematically in Fig. 6.
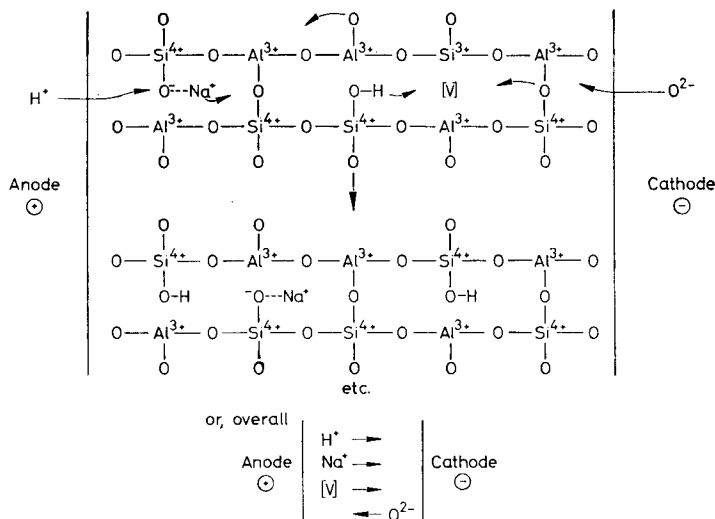
Fig. 6. Schematic representation of the proposed electrolysis mechanism

Although the alkali ions in the proposed mechanism clearly originate from the parent kaolinite material, the origin of the protons requires some comment. As in the case of vitreous silica [9], hydroxyl groups can be incorporated in the aluminosilicate glass during the flame fusion process. These hydroxyls are probably not those present in the original kaolinite, which had been dehydroxylated prior to fusion; identical hydroxyl intensities were recorded in the i.r. spectra of aluminosilicate glasses prepared from the anhydrous oxides by flame fusion. In addition to the inherited hydroxyl content, electrolysis in ambient laboratory air may also introduce hydroxyl groups at the anode [9]. Unlike the alkali ions, whose

final fate is clearly evident from X-ray diffractograms, the ultimate fate of the protons is not so obvious. Under the influence of the electric field gradient, the protons will be transported through the glass to the cathode where recombination with hydroxyls produces local concentrations of water acting as a nucleating agent produced *in situ*. Some evidence of this action is seen in the slightly improved crystallinity of the mullite underlying the kalsilite layer at the cathode. In connection with the migration of protons, the observed coalescence of bubbles and their migration to the cathode seems significant; this behaviour suggests either that the bubbles themselves are positively charged (possibly by virtue of their contents) or that they are dragged to the cathode by some charged species intimately associated with them but not contained by them, similar to the migration of voids during the sintering of polycrystalline solids. Since the electron microprobe results show that the bubbles are depleted of all metallic cations, it seems likely that at some stage the contents may have been water or its constituents. This conclusion also follows from the donor-acceptor theory of Taylor [15] in which water is lost from hydroxyl-containing solids by proton migration to regions which subsequently form pores (the donor regions). Under an electric field, protonic migration is to the cathode, leading to a high concentration of pores in that region as is observed to be the case.

The foregoing discussion is largely based on the work of Hetherington et al. [9] on Al-doped vitreous silica, and is therefore only strictly applicable to systems containing less Al than would be necessary to "saturate" the available tetrahedral network sites. When the alumina content exceeds this critical concentration as in the present case, the structure favours a two-phase system. The presence of additional alumina apparently does not affect the electrolysis mechanism, however, since, as in the case of low-aluminium glasses [9] migration of Al or Si could not be established by the electron microprobe in the present glasses. Preferential phase separation at the cathode therefore seems to be due solely to the transport of alkali ions and protons and is independent of aluminium content, provided the minimum amount of Al^{3+} for the formation of vacancy-containing centres is maintained.

The effect of applied voltage on the heat of reaction

Fig. 5 shows that, allowing for the considerable experimental error, an applied electric field of $\sim 5 \times 10^5$ V/m reduces the area of the devitrification exotherm by an amount corresponding to $2-7$ kcal/mol. The measured enthalpy of the reaction is related to the free energy change ΔG and entropy change ΔS by

$$\Delta H = \Delta G + T_1 \Delta S. \tag{1}$$

For the reaction in an electric field, the enthalpy, free energy and entropy changes now become ΔH_e, ΔG_e and ΔS_e; these are related by

$$\Delta H_e = \Delta G_e + T_2 \Delta S_e. \tag{2}$$

Since the average difference between T_1 (the reaction temperature in the absence of a field) and T_2 (the reaction temperature in the presence of a field) is about $10°$ in the present experiments, the change in $\varDelta G$ arising from this change in reaction temperature is estimated from free energy data for Al_2O_3 and SiO_2 to be less than 5%, i.e. negligible. The difference in the enthalpy change resulting from the application of a field is therefore:

$$\varDelta H - \varDelta H_e = (\varDelta G - \varDelta G_e) + (T_1 \varDelta S - T_2 \varDelta S_e). \qquad (3)$$

Since $\varDelta G$ refers to the free energy difference between the initial and final states (i.e. vitreous and crystalline states),

$$(\varDelta G - \varDelta G_e) = (G^c - G^v) - (G_e^c - G_e^v). \qquad (4)$$

where the superscripts c and v refer to the crystalline and vitreous state respectively. Now in an electric field E,

$$G_e = G - (V/4\pi)\varepsilon E^2 \qquad (5)$$

where V is the volume of material of dielectric constant ε [16]

$$(\varDelta G - \varDelta G_e) = -(V/4\pi)E^2(\varepsilon^v - \varepsilon^c). \qquad (6)$$

Electrical measurements on the $Al_2O_3 - SiO_2$ system [17] show that although a discontinuity in conductance sometimes occurs at the devitrification temperature, the capacitance of the system remains virtually constant, suggesting that $\varepsilon^v \approx \varepsilon^c$. This is confirmed by the reported values of dielectric constant for a series of commercial aluminosilicate glasses which fall in the range $5.9 - 7.2$ [18], in excellent agreement with the range of values reported for mullite porcelains ($6.2 - 6.8$ [19]); these porcelains are of similar composition to the devitrified glass (i.e. containing mullite and crystalline silica in a vitreous matrix). Thus, if $\varepsilon^v \approx \varepsilon^c$, the term $(\varDelta G - \varDelta G_e)$ in Eq. 6 approaches zero, and therefore since $\varDelta H$ and $\varDelta G$ are assumed to be independent of temperature, and $T_1 \approx T_2$, the change in free energy of the system due to the applied field will be negligible compared with the change in entropy induced by the field, which must therefore account almost entirely for the field-induced change of enthalpy. Since the structure of the glass can be considered to be a random network containing Al and Si, the effect of the field will be to reduce the randomness of the system, i.e. $(T\varDelta S - T\varDelta S_e)$ should become increasingly more positive with increasing field strength. Since the recrystallization reaction is spontaneous and exothermic, $\varDelta H$ and $\varDelta G$ are both negative; in the presence of the field $\varDelta H$ will become less negative, as is observed experimentally. The observed change in $\varDelta H$ caused by a field of $\sim 5 \times 10^5$ V/m corresponds to an entropy change of about $2 - 5$ e.u., assuming that the field has no effect on $\varDelta G$. Theoretical calculations of disorder entropy in aluminosilicates [20] show that the molar entropy change of a mullite-like phase in which a random network of octahedral Al ions becomes completely ordered is of the order of 10 e.u. Thus, within the limitations of the experiment and the approximations used in the theoretical

entropy calculations, the field-induced change in the heat of recrystallization involves an entropy change of similar order to that involved when a disordered mullite-like material becomes more regular. This should not, however, be taken to mean that the electric field acts only on the octahedral regions of the glass; the present experiments give no information on this point.

Conclusions

Electric fields reduce the DTA peak temperature for the exothermic devitrification of aluminosilicate glass derived from kaolinite, and lead to the formation of alkali aluminium silicates at the cathode. The principal migrating species are the alkali metal ions; a postulated electrolysis mechanism also involves the movement of protons, for which some evidence is provided by the accumulation at the cathode of numerous bubble-like voids. The distribution of other network-forming constituents throughout the sample is unaffected by the field.

Provided the DTA peak temperature and electrolysis starting temperature are not too close, the peak temperature is unaffected by varying the temperature at which electrolysis is commenced, even though localised electrical heating occurs when the voltage is applied under conditions in which the charge carriers are mobile.

The heat of the exothermic reaction is reduced by electric fields due to a decrease in the entropy of the system; the free energy change is virtually unaltered by the field.

*

References

1. J. F. MacDowell and G. H. Beall: J. Amer. Ceram. Soc., 52 (1969) 17.
2. R. C. deVekey and A. J. Majumdar: Nature, 225 (1970) 172.
3. K. J. D. MacKenzie, J. App. Chem., 20 (1970) 80.
4. M. F. Coleman, J. F. Duncan and D. N. Sitharamarao, Rev. de Chim. Minerale, 7 (1970) 1129.
5. K. J. D. MacKenzie: Trans. J. Brit. Ceram. Soc., 72, (1973) 209.
6. Report of the Commission on Physicochemical Measurements and Standards of the Physical Chemistry Division, Pure and Applied Chem. 29 (1972) 597.
7. P. S. Nicholson and R. M. Fulrath: J. Amer. Ceram. Soc., 53 (1970) 237.
8. K. J. D. MacKenzie: J. Thermal Anal., 5 (1973) 19.
9. G. Hetherington, K. H. Jack and M. W. Ramsay: Phys. Chem. Glasses, 6 (1965) 6.
10. K. J. D. MacKenzie and I. W. M. Brown: Phys. Chem. Glasses, 16 (1975) (in press),

11. C. W. BURNHAM: Carnegie Inst., Washington, Yearbook, 63 (1963—4) 223.
12. (a) J. W. CAHN: J. Chem. Phys., 42 (1965) 93.
    (b) J. W. CAHN and R. J. CHARLES: Phys. Chem. Glasses, 6 (1965) 181.
13. R. W. HOPPER and D. R. UHLMANN: Phys. Chem. Glasses, 14 (1973) 37.
14. D. KASHCHIEV, J. Crystal Growth 13/14 (1972) 128.
15. H. F. W. TAYLOR: Clay Min. Bull., 5 (1962) 45.
16. E. A. GUGGENHEIM, Thermodynamics, 4th Ed, North-Holland, Amsterdam, 1959, p. 412.
17. I. W. M. BROWN and K. J. D. MACKENZIE: In preparation.
18. A. M. ALPER (Ed.): High Temperature Oxides, Part IV, Academic Press, New York, 1971, p. 9.
19. F. SINGER and S. S. SINGER: Industrial Ceramics, Chapman and Hall, London (1963), p. 1179.
20. J. K. D. MACKENZIE and J. F. DUNCAN: Trans. Brit. Ceram. Soc., 70 (1971) 181.

RÉSUMÉ — En combinant les techniques d'ATD et d'électrolyse, on montre que l'effet d'un champ électrique entraîne la diminution de la température de dévitrification (phénomène exothermique) des verres aluminosilicatés dérivés de la kaolinite. Cet abaissement de température peut atteindre 30°. Il se forme à la cathode une couche cristalline de silicate d'aluminium alcalin par suite de la migration des ions des métaux alcalins vers cette électrode. En dessous, on trouve de la mullite avec de nombreuses cavités ressemblant à des bulles d'air.

L'électrolyse ne change pas la distribution de l'aluminium et du silicium. Les résultats peuvent être interprétés en faisant appel à un mécanisme d'électrolyse comprenant une migration coopérative des ions alcalins et des protons vers la cathode. La diminution de la température de dévitrification sous l'effet du champ électrique est attribuée à la diminution de l'entropie du système soumis à l'électrolyse.

ZUSSAMMENFASSUNG — Eine Kombination der Elektrolyse und von DTA zeigt, daß ein elektrolytisches Feld zur Verminderung der Devitrifikationstemperatur von kaolinitbasischen Aluminiumsilikatgläsern beeinträchtigt. Diese Verminderung kann 30° betragen. Infolge der Wanderung der Alkalimetallionen bildet sich auf der Kathodenfläche eine kristallene Decke aus; darunter befindet sich Mullit mit zahlreichen luftblasenähnlichen Höhlungen. Die Elektrolyse beeinflusst nicht die Verteilung des Al-s und Si-s. Die Erscheinung läßt sich durch einen elektrolytischen Mechanismus beruhend auf die Wanderung der Alkaliionen und der Protonen zur Kathode erklären. Die Verminderung der Devitrifikationswärme im elektrischen Feld läßt sich auf eine Verminderung der Entropie des Systems unter Elektrolyse zurückzuführen.

Резюме — На примере комбинированного метода ДТА — электролиз было установлено, что действие электрических полей вызывает уменьшение температуры экзотермического расстекловывания алюминосиликатных стекол, производных каолинита, до 30°. Вследствии миграции ионов щелочного металла к электроду, на катоде образуется слой экстремально кристаллического щелочно-алюминиевого силиката. Нынешний слой содержит муллит и пузыркого-подобный пустот в высокой степени концентрации. Распределение Al и Si не изменяется при электролизе. Полученные результаты интерпретированы на основе механизма электролиза, включающий совместную миграцию ионов щелочного металла и протонов к катоду. Наблюдаемое понижение теплоты расстекловывания при действии электрического о поля обусловлено понижением энтропии в электролизной системе.