JOURNAL OF MATERIALS SCIENCE 24 (1989) 2884–2890

Dielectric properties of R_2O–SiO_2 glasses prepared via sol–gel

M. A. VILLEGAS, J. R. JURADO, J. M. FERNÁNDEZ NAVARRO
Instituto de Cerámica y Vidrio, CSIC Arganda del Rey, Madrid, Spain

Gels from R_2O–SiO_2 (R = potassium, sodium and lithium) systems with a maximum alkaline content of 5 mol % were prepared. The conductivity and the alkaline ion incorporation degree as a function of temperature were studied by a.c. impedance spectroscopy and dielectric relaxation measurements. At low temperature (20 to 200° C) the major contribution to the total electric conductivity is due to water conducting species (mainly protons) which are adsorbed inside the gels. From 450° C gels start to behave as conventional glasses. The total electric conductivity and activation energy values for conduction at those high temperatures are of the same order as those for glasses prepared by direct melting.

1. Introduction

A large variety of superionic conductors can be prepared thanks to the low temperature polymerization technique [1].

To prepare glasses via sol–gels, it is necessary to incorporate water during the first step of the sol preparation in order to hydrolyse the alkoxide precursors of the final oxides. Therefore, materials obtained via sol–gel have numerous water molecules adsorbed as well as silanol groups [2, 3] which make it difficult for alkaline ions to be incorporated into the gel structure [4, 5].

Preliminary electrical conductivity results on $5R_2O.95SiO_2$ gels [6] indicated higher total conductivity than that of similar compositions prepared by melting. This high conductivity at low temperature is due to the water conducting species (mainly proton conduction); however, the alkaline ions play an important role in the proton motion. There are few reports assuming high conductivity values at room temperature for gels and the values obtained in these experiments were attributed to the alkaline ions instead of the protons [7, 8]. Nevertheless, Hayri and Greenblatt [9] attributed the high conductivity values measured at low temperature to a proton conduction mechanism.

The present work deals with detailed electrical conductivity measurements using a.c. impedance spectroscopy and dielectric relaxation methods to determine both the electrical behaviour and the effect of alkaline ions in the electrical conduction mechanism.

2. Experimental details

2.1. Sample preparation

Tetraethylorthosilicate (TEOS) and lithium, sodium and potassium nitrates were used as precursors to prepare sols. In order to hydrolyse the silicon alkoxide, a mixture of HCl and $HOOC$–CH_3 was used as catalyst and 2-propanol was employed as the common solvent. The molar ratio TEOS : H_2O : 2-propanol was 1 : 10 : 2 and the final pH of the sols was approximately 2. Thin slabs (1 to 3 mm) were obtained from the sols. Gelation was carried out in Petri glass dishes. Silica slabs were also prepared in a similar way.

Sols gelled at 60° C in the course of several hours in a forced air oven. Samples were dried at that temperature for several days and then heat-treated at 1.25° C min^{-1} up to 120 and 200° C with a stabilization time of 1 h at 120 and 200° C. The compositions studied are listed in Table I.

2.2 Electrical measurements

Slabs of approximately 1 to 3 mm thickness and 6 to 8 mm^2 surface area were employed to record the complex impedance spectra and dielectric relaxation peaks. High conductivity silver paste was employed to form contact electrodes. It was deposited onto both sides of the specimens. The samples were dried at 120° C for 2 h in order to remove the organic component of the paste. A.c. electrical measurements were carried out with an impedance analyser HP model 4192 A connected to a computer HP model 9000-216.

Specimens for electrical measurements were placed inside a hot sample holder with an accurate temperature control. Every impedance spectrum was recorded after, at least, 15 min of temperature stabilization. The heating and cooling rate was 3° C min^{-1} from 25 to 200° C in steps of 25° C. Values were collected during heating and cooling in order to obtain reproducible measurements.

TABLE I Compositions studied in the R_2O–SiO_2 system and of pure silica (mol %)

Sample	Li_2O	Na_2O	K_2O	SiO_2
SiO_2	–	–	–	100
1.1	–	–	5	95
1.2	–	5	–	95
1.3	5	–	–	95
2.1	–	1	–	99
2.2	–	2	–	98

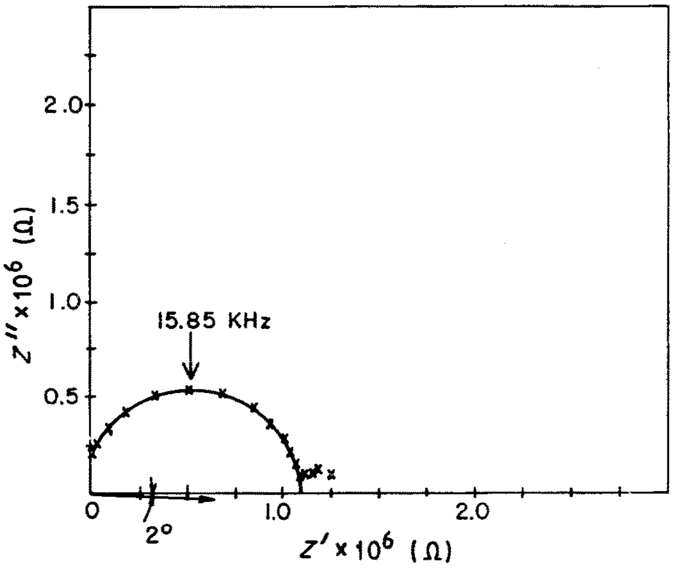

Figure 1 A.c. impedance spectrum of the pure silica sample at 25° C.

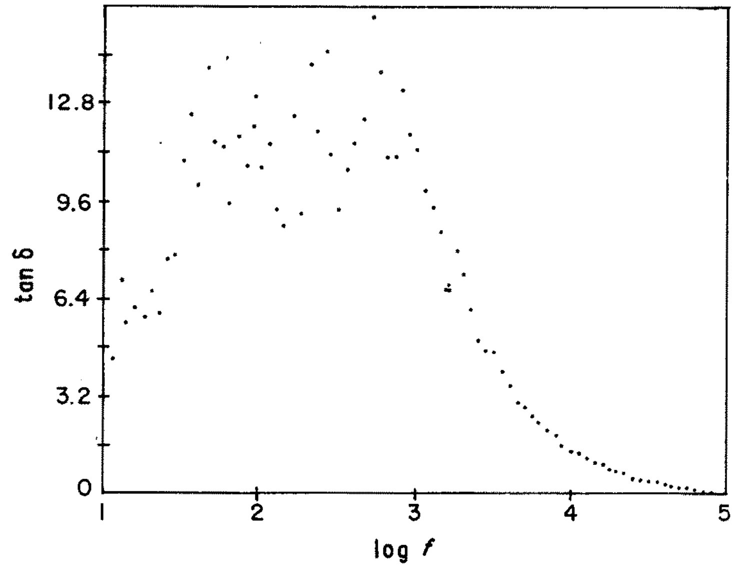

Figure 2 Dielectric relaxation spectrum of the pure silica sample at 25° C.

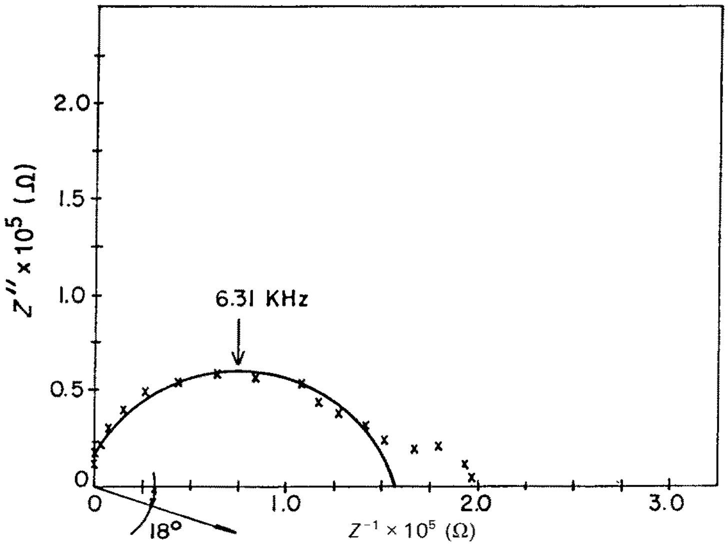

Figure 3 A.c. impedance plot of sample 1.1 ($5K_2O.95SiO_2$) at 25° C.

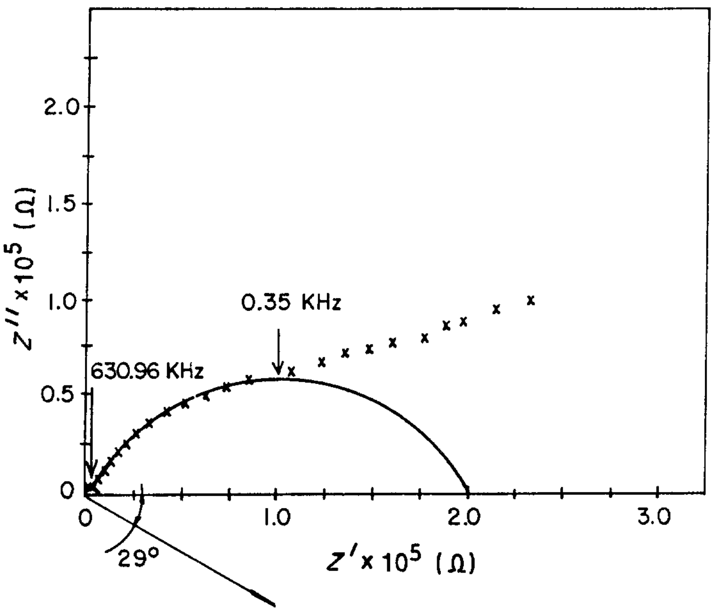

Figure 4 A.c. impedance plot of sample 1.2 ($5Na_2O.95SiO_2$) at 25° C.

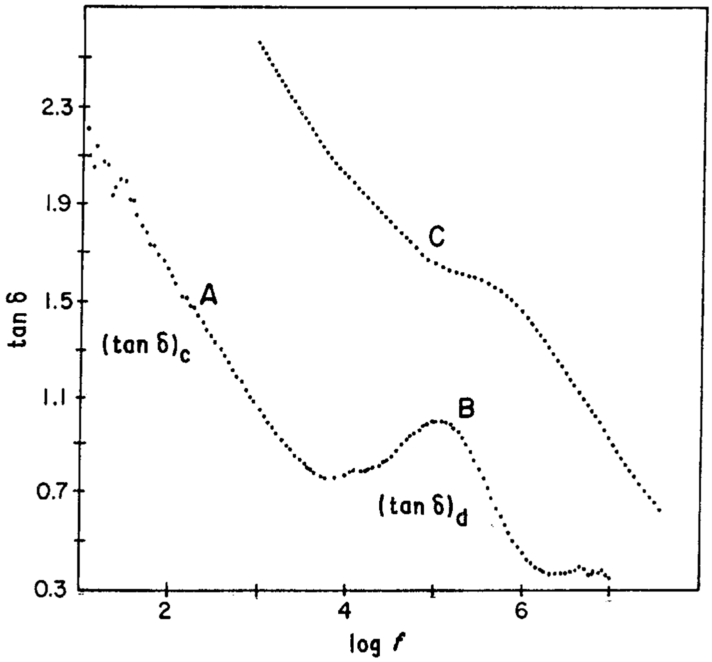

Figure 5 Dielectric relaxation plot of sample 1.2 ($5Na_2O.95SiO_2$) at 25° C.

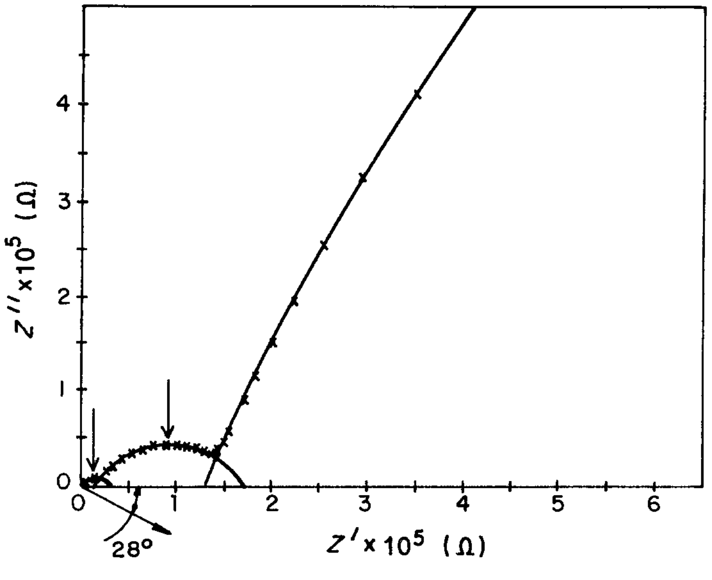

Figure 6 A.c. impedance spectrum of sample 1.3 ($5Li_2O.95SiO_2$) at 155° C.

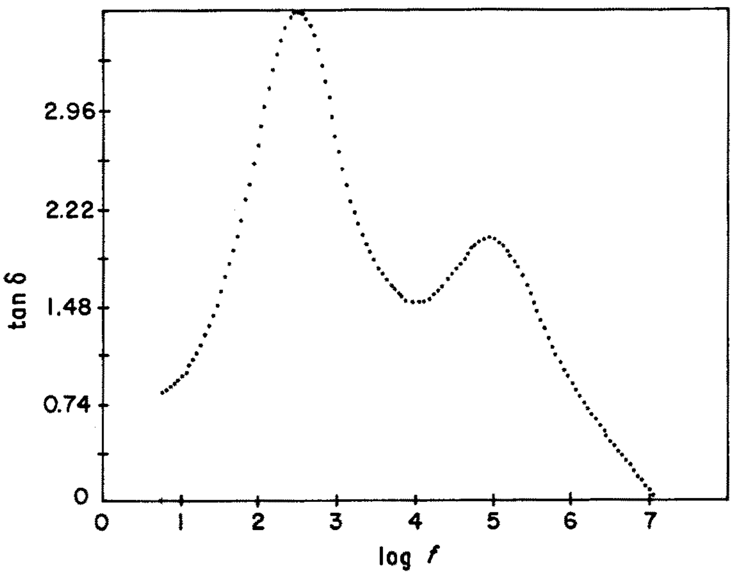

Figure 7 Dielectric relaxation peaks of sample 1.3 ($5Li_2O.95SiO_2$) at 155° C.

3. Results and discussion

Fig. 1 shows the impedance spectrum of the pure silica gel, which exhibits one arc associated to the interior material resistance. This is the only contribution to the total resistance of the circuit. The arc presents a depression angle α of 0°, approximately, which indicates an ideal dispersion plot. As the temperature was raised, α was kept nearly constant, while the conductivity (which was calculated from the impedance value of the semicircle intersection with the real axis Z') decreased from $8.85 \times 10^{-7}\,\Omega^{-1}\,cm^{-1}$ at 25° C to $1.48 \times 10^{-7}\,\Omega^{-1}\,cm^{-1}$ at 75° C. At higher temperatures it was not possible to detect any signal. This indicates the elimination of water conducting species. The large content of water in the pure silica sample is removed at a temperature around 100° C. The dissipation factor (tan δ) (Fig. 2) indicates a decrease of tan δ from 10^3 Hz. This occurs in the case of heterogeneous systems where two or more phases are present. At lower frequencies a wide band is observed, which indicates an overlapping of tan δ curves and non-Debye behaviour.

Sample 1.1 ($5K_2O.95SiO_2$) shows a different behaviour: the water effect was not observed up to 125° C. Below this temperature it was impossible to detect any signal of conductivity. Fig. 3 shows one arc with a depression angle of about 18°, higher than that of pure silica gel. The conductivity at 125° C is $6.09 \times 10^{-6}\,\Omega^{-1}\,cm^{-1}$ and then decreases at 200° C, whereas α increases slightly. No peaks were noticed in the tan δ against frequency curves. This fact may be accounted for by the K^+-ions being incorporated into a pure silica gel thus yielding a structural or geometrical modification of the gel, rather than a direct participation in the conduction mechanism. The alkaline ions could modify the paths where protons and other ions can move freely. The large size of K^+-ion makes the motion of the conducting species in the temperature range of 25 to 125° C difficult. From this temperature, K^+-ions cannot prevent movement of the water ions, and above 200° C the conductivity disappears due to the almost total removal of water from the gels.

Nevertheless, the incorporation of Na^+-ions causes a different situation to that with K^+-ions as is shown in Fig. 4. Two overlapping arcs are present; the high frequency arc could be attributed to the silica matrix, whereas the intermediate arc may be due to a combined effect between the geometrical morphology of the particles and/or the phases present in the gel. The dissipation factor spectrum of Fig. 5 shows a peak at

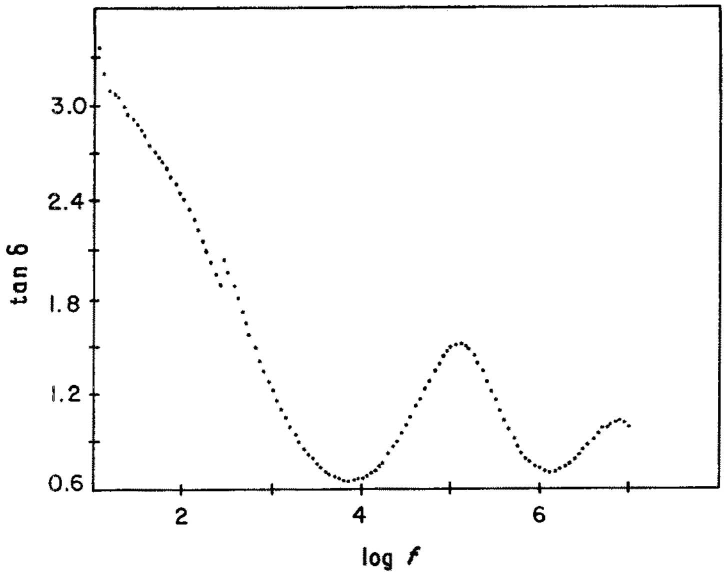

Figure 8 Dielectric relaxation peaks of sample 2.2 ($2Na_2O.98SiO_2$) at 25° C.

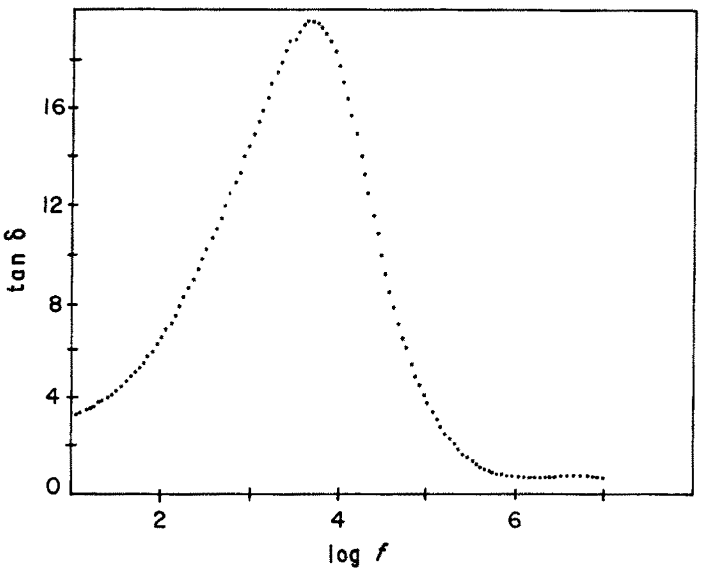

Figure 9 Thermal evolution of the dielectric relaxation peak of sample 2.2 ($2Na_2O.98SiO_2$) at 150° C.

10^5 Hz. The regions A and B indicate a typical dipolar relaxation behaviour: A indicates the effect of dielectric loss of conduction, and B corresponds to a process of dipolar reorientation relaxation. It is probable that the dipole formation in these gels, particularly water dipoles, together with alkaline ions (Na^+) could contribute to it. Therefore, water dipoles or more unlikely Na^+-water dipoles could be responsible for the behaviour observed in Fig. 5. On the other hand, the Na^+-ions, due to geometrical reasons, contribute to modify the gel structure favouring the motion of conducting species. From 150° C the gel conductivity clearly vanishes and at 200° C it disappears.

Fig. 6 shows the impedance spectrum of sample 1.3 at 155° C. In this spectrum compared to that of Na^+-containing gel, the presence of three arcs can be observed more clearly. In actual fact, the low frequency arc is not a semicircle which could be due to an interface electrode-gel, such as it is described in some electrolyte ceramics. The high and intermediate frequency arcs correspond to the total gel response, and it seems to indicate that several phases and their geometries in the gel microstructure, play a role in the total conduction pattern. The relaxation spectrum of Fig. 7 is a striking feature of this gel. Two peaks of tan δ against frequency are clearly seen: one at $\sim 10^2$ Hz and the other at $\sim 10^5$ Hz, which could be accounted for by two combined dipolar effects. This is due to the existence of dipoles of different nature in the gel. Similar behaviour was detected in gels containing Na^+-ions (see Fig. 5). In addition, in the gel 2.2 ($2Na_2O.98SiO_2$) (Fig. 8) two peaks at $\sim 10^5$ and at $\sim 10^7$ Hz were observed, both probably due to a new type of dipole reorientation. When temperature is increased an overlapping peak was detected in all gels, as is illustrated in Fig. 9. The signal disappears at 200° C in all cases.

With regard to the gels investigated it can be said, with the exception of both K^+-containing gel and that of pure silica, that all the gels have the same a.c. impedance behaviour and similar relaxation mechanism. Therefore, the effect produced by Na^+- and Li^+-ions could be considered the same. Table II shows the conductivity values at 25, 50 and 150° C; data reported by other authors [8] are also included. The incorporation of alkalis into a pure silica matrix increases, of course, the total conductivity. Despite Ravaine *et al.*'s suggestions [8], the alkaline ions modify the conduction paths and the water ions can easily move through them. Ravaine *et al.* [8] carried out the conductivity measurements in dry air, however, these conductivity values are very close to the data obtained in this work

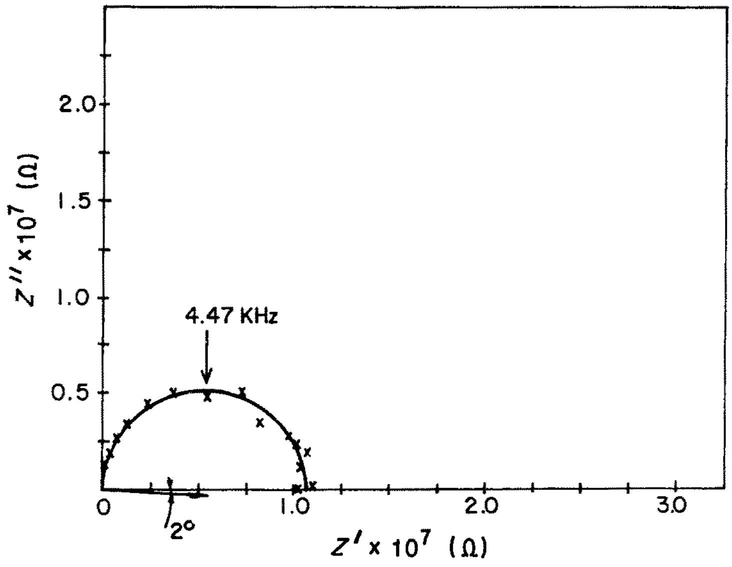

Figure 10 A.c. impedance plot of sample 2.2 ($2Na_2O.98SiO_2$) at 475° C.

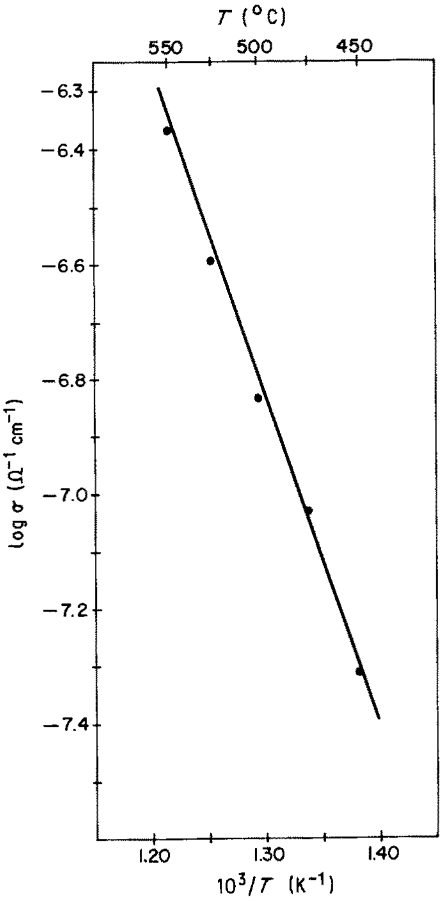

Figure 11 Arrhenius plot for sample 2.2 ($2Na_2O.98SiO_2$).

TABLE II Electrical conductivity values $\sigma(\Omega^{-1}\,cm^{-1})$ from complex impedance plots of the R_2O–SiO_2 samples. The values in which the order of the arc is not indicated correspond to the cases in which only one arc exists

Sample	σ(25° C)	σ(50° C)	σ(150° C)
SiO_2	8.88×10^{-7}	1.75×10^{-7}	$\ll 10^{-8}$
1.1	–	–	9.52×10^{-6} (1st arc)
1.2	1.90×10^{-4} (2nd arc)	1.51×10^{-6}	6.82×10^{-7} (2nd arc)
1.3	5.13×10^{-4} (2nd arc)	5.91×10^{-5} (1st arc)	2.56×10^{-6} (1st arc)
2.1	2.73×10^{-4} (2nd arc)	4.61×10^{-4} (2nd arc)	2.16×10^{-6} (1st arc)
2.2	2.53×10^{-5} (2nd arc)	2.21×10^{-5} (2nd arc)	1.10×10^{-4} (2nd arc)
SiO_2*	1.4×10^{-9}		
$SiO_2 + Li_2O$*	2.3×10^{-5}		

*samples and values from Ravaine *et al.* [8].

in similar gels. The conductivity pattern attributed by those authors to the Na^+- and Li^+-ions, in comparison with the present results, could be due to the adsorbed water ionic species (particularly to the proton conduction). That is in agreement with the suggestions of Hayri and Greenblatt [9].

A gel could be considered as a heterogeneous dielectric where silica particles are surrounded by water molecules, which largely modify the dielectric relaxation spectrum of the gel. Na^+- and Li^+-ions in the samples produce a significant structural and microstructural modification of the gels, which allows the ionic motion. However, the presence of K^+-ions makes the mobility of the ions that govern the conduction mechanism difficult. Ravaine *et al.* [7, 8] suggested that gels have a similar structure to conventional glasses obtained by melting. Both glasses prepared by melting and gels with identical chemical composition, show similar structures when the residual chemical and physical adsorbed water is removed from the gels. In order to demonstrate this point, sample 2.2 was heat-treated at temperatures higher than 200° C within the conductivity hot sample holder. The first clear signal appeared at 450° C, and Fig. 10 shows the a.c. impedance spectrum at 475° C. One arc and its conductivity value of $9.35 \times 10^{-8}\,\Omega^{-1}\,cm^{-1}$ were obtained. This conductivity value is of the same order as that of the conventional glass with low alkaline ion content. Fig. 11 shows the Arrhenius plot (log σ against $1/T$) for the gel 2.2. Linear behaviour in the temperature range tested can be observed, which is normally attributed to a melting glass pattern. The calculated activation energy for conduction was 1.10 eV which is in close agreement with those of alkaline silicate glasses (Fig. 12). Therefore, it could be said that in the temperature range of 25 to 400° C the conduction mechanism and the dielectric relaxation process in gels are governed by the presence of molecular groups and derived species from water. From 450° C alkaline ion conduction is predominant.

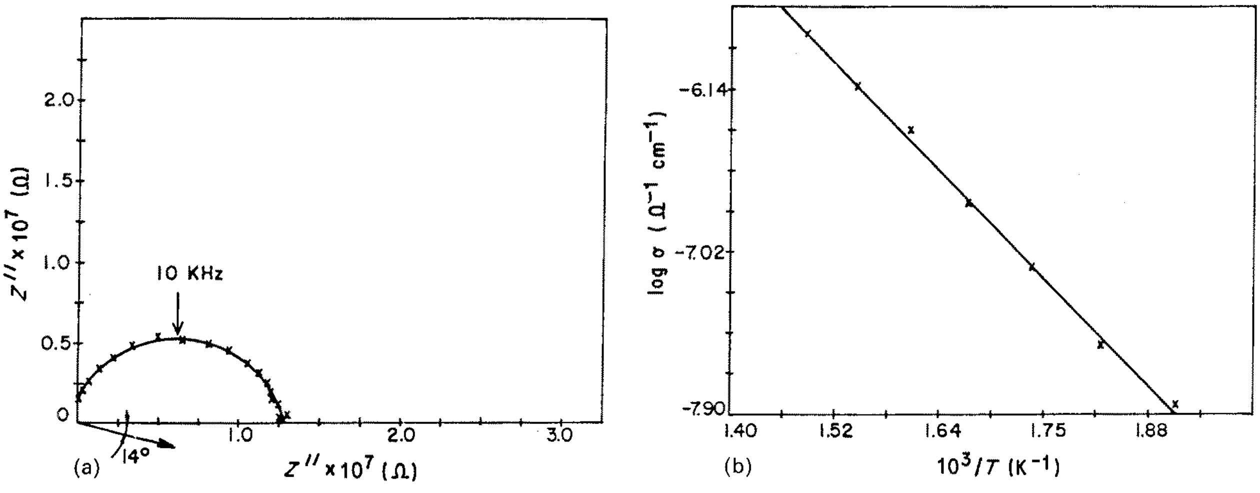

Figure 12 (a) A.c. impedance plot of an insulator conventional glass at 400° C and (b) Arrhenius plot of an insulator conventional glass, $E_a = 0.96\,eV$.

4. Conclusions

The vitreous materials obtained by the sol–gel method show, at low temperature, noticeable electrical conductivity values, higher than those of conventional glasses of the same composition. The most important contribution to the conductivity is due to the ionic species of water, particularly to the proton conduction. The alkaline ions are not properly incorporated in the vitreous structure. They are weakly bound to the gel structure and favour the proton motion. They are incorporated when molecular adsorbed water is removed from the gels and when dehydration of silanol groups is achieved. From 450° C the alkaline ions are found to be bound to the glass network in a similar way to those in conventional glasses prepared by melting.

References

1. J. P. BOILOT and Ph. COLOMBAN, *J. Mater. Sci. Lett.* **4** (1985) 22.
2. E. M. RABINOVICH, *J. Mater. Sci.* **20** (1985) 4259.
3. D. L. WOOD, E. M. RABINOVICH, D. W. JOHNSON, Jr., J. B. MACCHESNEY and E. M. VOGEL, *J. Amer. Ceram. Soc.* **66** (1983) 693.
4. M. A. VILLEGAS and J. M. FERNANDEZ NAVARRO in Proceedings of the First International Workshop on Non-Crystalline Solids, San Feliú, May 1986, edited by M. D. Baró and N. Clavaguera (World Scientific Publishing, Philadelphia, 1986) p. 433.
5. M. A. VILLEGAS and J. M. FERNANDEZ NAVARRO, *J. Non-Cryst. Solids* **100** (1988) 453.
6. M. A. VILLEGAS and J. M. FERNANDEZ NAVARRO, *Bol. Soc. Esp. Ceram. Vidr.* **26** (1987) 235.
7. D. RAVAINE, J. TRAORE, L. C. KLEIN and I. SCHWARTZ, *Mater. Res. Soc. Symp. Proc.* **32** (1984) 139.
8. D. RAVAINE, A. SEMINEL, Y. CHARBOUILLOT and M. VINCENS, *J. Non-Cryst. Solids* **82** (1986) 210.
9. E. A. HAYRI and M. GREENBLATT, *ibid.* **94** (1987) 387.
10. S. P. MUKHERJEE, *ibid.* **42** (1980) 477.
11. S. P. MUKHERJEE, J. ZARZYCKI and J. P. TRAVERSE, *J. Mater. Sci.* **11** (1976) 341.
12. M. C. WEINBERG and G. F. NEILSON, *ibid.* **13** (1978) 1206.

Received 19 February
and accepted 11 October 1988