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# Dielectric Measurements on Lithium Silicate Glasses

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The static dielectric constant of some lithium silicate glasses has been measured at temperatures down to −145°C. A step is observed in the dielectric constant at low temperatures for glasses for which a component line of lowest activation energy is observed in the NMR spectra of $^7$Li. A motion of lithium ions within limited regions is presumed to be responsible for this polarizational effect as well as for the motional narrowing effect upon the component line of lowest activation energy in the NMR spectra.

NMR measurements have shown that lithium ions are present in at least two different positions in lithium silicate glasses.[1] From the temperature-dependent line narrowing of the $^7$Li-resonance two different values of the activation energy for the diffusional movement of the lithium ions have been determined. A larger value around 0.20 eV is attributed to the diffusion of cations in alkali-rich clusters and a smaller value around 0.10 to 0.12 eV to a movement of the ions within restricted regions. Activation energies have also been determined from electric measurements.[2] These investigations have also given two sets of data, one value around 0.62 eV assigned to a diffusion within clusters, and one larger value around 1.30 eV due to a diffusion of lithium ions through the silica matrix. The lower activation energy observed in the NMR measurements has thus no counterpart in the results of the other measurements. We have for this reason performed dielectric measurements on lithium silicate glasses at temperatures below room temperature where such measurements have not been made previously.

The experiments have at present been limited to the determination of the static dielectric constant. A Keithley 610 BR electrometer was used to measure the electric charge stored in a condenser of circular plates 10 mm in diameter. The condenser plates were mounted on a micrometer screw and the gap of the condenser ($d$) was adjusted to fit the different samples. This arrangement also facilitated the determination of the stray capacity of the condenser, for which a rather large correction has to be introduced, when the dielectric constant is determined. For the empty condenser the capacitance varies quite linearly with $1/d$, and we could determine quite accurately the theoretical capacitance

of the condenser from the slope of this line. Magnetically operated vacuum reed relays of an isolating resistance larger than $10^{15}$ ohms were used to switch the condenser from charging by a direct-current source to discharge through the electrometer. The reproducibility of these electric measurements is better than 1 %. Larger variations up to 3 % are observed between samples of the same charge of glasses of low alkali content. These discrepancies may be due to heterogeneities of the glass samples or to small variations in the preparation procedure. To improve the accuracy of the measurements the methods for the preparation of samples have to be revised first of all. Temperature was controlled by passing pre-cooled dry nitrogen gas through a specimen chamber containing the condenser. The plates of the condenser were mounted on teflon plugs, 1 cm high. This simple arrangement brought about sufficient thermal isolation to guarantee that temperature variations over the sample were less than 1°C. Sample preparation was done in accordance with the procedure used earlier in connection with the NMR measurements.[1] For the dielectric investigations all samples were first quenched between metal blocks, and the preparations which were thinnest were selected for the measurements. The samples were further ground to give quite parallel edges.

Some of the experimental results are shown in Figs. 1—3. The dielectric constant shows a characteristic step at a temperature around —90°C for those samples where a narrow component line is observed at room temperature in the NMR spectra of the $^7$Li-resonance. This shows that there exists at low temperature a loss peak associated with the motional mechanism responsible for the motional narrowing effect upon the narrow line of the NMR spectra. The results of our measurements are reproduced only up to room temperature in the figures. The dielectric constant grows very rapidly at higher temperatures due to the diffusional movement of cations inside the clusters. Glasses of high alkali content have here also a significant conductivity. Determination of a static dielectric constant is here impossible because the amount of charge stored on the condenser plates is dependent upon the time of charging and because the discharging procedure takes a very long time. At temperatures below room temperature relaxation effects do not influence the measurements to such a high degree. All the measurements have been made here according to a simple standard procedure where the condenser was charged for one minute, and the deflection of the electrometer was read 1 min after the discharge. The data thus obtained are shown by the solid line in the figures. The results of the measurements were not affected by the use of larger time limits for these operations. The electrometer deflection was also read ten seconds after discharge, which data are reproduced by the dotted line of the figures. The two different readings coincide well in regions where the dielectric constant is not dependent upon temperature. A reproducible divergence is observed at the characteristic step at —90°C, which indicates the presence of a relaxation phenomenon here. Dielectric phenomena of similar type have been observed at low temperatures in doped ionic crystals where the foreign ions are substituted for ions of larger size.[3,4] The very great similarity of the measurements on these crystals and on the lithium silicate glasses may support the assumption that lithium ions are free to move between alternative sites within a void in the glass samples as well.

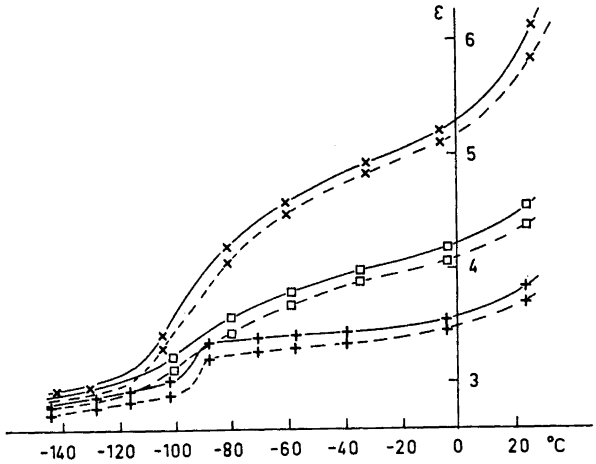


*Fig. 1.* Static dielectric constant of a glass containing 12 mole % $Li_2O$ and 88 mole % $SiO_2$. × Quenched glass; □ Annealed glass 30 min at 600°C; + Annealed glass 2 hours at 650°C.

The step at −90°C for the low alkali glasses is seen most clearly for the sample containing 12 mole % $Li_2O$ (Fig. 1). The step is not so steep for glasses of lower alkali content and the growth of the dielectric constant occurs here within a larger interval of temperature from −120°C to about −20°C. We will assume that these glasses have been quenched less effectively, which may be due to their higher viscosity. The NMR spectra reveal a similar effect as a line

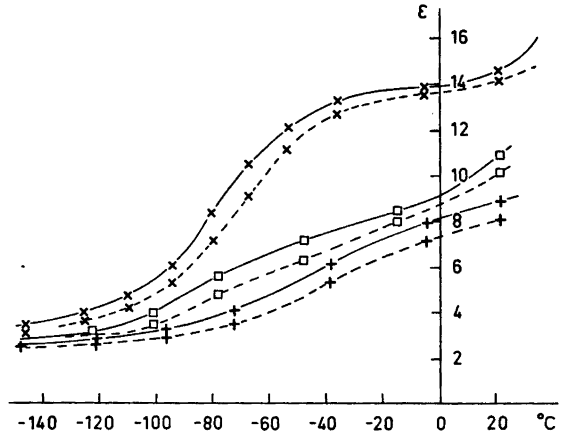


*Fig. 2.* Static dielectric constants of quenched glasses of the compositions: × 24 mole % $Li_2O$, 76 mole % $SiO_2$; □ 22 mole % $Li_2O$, 2 mole % CaO, 76 mole % $SiO_2$; + 22 mole % $Li_2O$, 2 mole % $K_2O$, 76 mole % $SiO_2$.

of intermediate width is observed for the quenched glass containing only 6 mole % $Li_2O$. The height of the step is reduced in all of the low alkali glasses upon heat treatment. A very small step also seems to remain, however, after hours of heat treatment.

A step in the dielectric function is also observed at low temperatures for the pure lithium silicate glasses of the high alkali range (Fig. 2). Here the step is centered around −70°C, that is, at a temperature some 20 degrees higher than for the glasses of the low alkali range. This coincides with the observation of an activation energy of the narrow component line for the high alkali glasses which is somewhat higher than for the low alkali samples. The step for glasses with a $Li_2O$ content less than 30 mole % is clearly resolved from the step in the dielectric function, which is observed near room temperature for all glass samples. For glasses of the highest contents of $Li_2O$ the resolution is not quite clear. The temperature limits for the motional processes are here probably shifted a little towards each other.

The step at −70°C is effectively eliminated by the addition of only small amounts of potassium or alkali-earth ions to the glass. It could be assumed that the growth of the dielectric constant due to the diffusional movement of cations inside the clusters is also shifted towards higher temperatures for the three component glasses. We have, however, not been able to observe any resolution between the two steps of the dielectric function for these glasses, for which two component lines are registered in the NMR spectra. The dielectric measurements reveal, in accordance with the NMR investigations, that the effects upon substitution of lithium ions by other ions are not greatly dependent upon the nature of the substituents for glasses in the high alkali range. Only for three-component glasses of very low content of lithium (6 mole % of $Li_2O$) is a difference observed in the NMR spectra between glasses

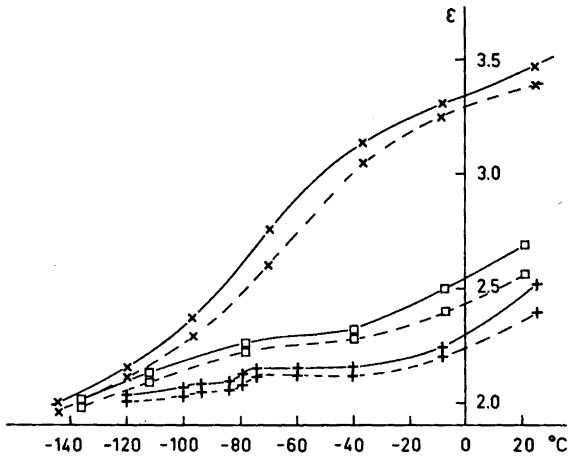


*Fig. 3.* Static dielectric constant of a glass containing 6 mole % $Li_2O$, 24 mole % CaO, 70 mole % $SiO_2$. × Quenched glass; □ Annealed glass, 30 min at 600°C; + Annealed glass, 2 hours at 650°C.

containing potassium and calcium. A quite corresponding pattern is observed in the dielectric measurements (Fig. 3). For glasses containing potassium no step is observed in the dielectric constant below room temperature, whereas quenched glasses containing calcium display an appreciable step between −100°C and −50°C. This step is eliminated upon heat treatment of the glass, which is quite in accordance with the conditions for the low alkali glasses.

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