

A Nuclear Magnetic Resonance Study of Diffusion in Lithium Silicate Glasses

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From the shape of the NMR resonance of ${}^7\text{Li}$ the presence of lithium ions in small groups included in voids in the silica-rich network as well as in larger clusters of higher than average alkali content is demonstrated. The activation energy for the diffusion of the cations, as determined from the temperature dependence of the line width, is much smaller for the lithium ions placed in the silica-rich matrix than for the clustered ions. It is concluded that the lithium ions of the silica-rich phase exhibit a thermal motion within cavities of the silica matrix. This type of thermal motion does not contribute to the overall material transport, for which process higher activation energies are observed. The size of the activation energies for the two types of lithium ions is increased appreciably on addition of other alkali ions and alkaline-earth ions to the glass. It is supposed that this effect is due to a tightening of the glass structure.

The vitreous two-component systems of lithium oxide and silica exhibit many physical properties which vary greatly with the composition and the thermal history of the glass. This condition has been explained by the assumption of different positions for the lithium ions in the glass. We have assumed that further insight into the underlying structural relationships could be gained from studies of diffusion processes of the lithium ions, and we have therefore investigated the motional narrowing effect upon the ${}^7\text{Li}$ nuclear magnetic resonance for a number of lithium silicate glasses. Such NMR measurements allow us to determine the size of the activation energy of the spin diffusion process, which quantity is most helpful in characterizing the positions of the cations.

It is a well-known fact that the tendency towards the formation of a non-uniform distribution of cations in the glass structure increases with the field strength of the ions. The largest effect thus appears for ions of a high charge and/or small ionic radius. The lithium silicate system is therefore very suitable for the study of such effects. The NMR signal is here also comparatively intense as the dominating isotope of lithium has a large magnetic moment and a comparatively small quadrupole moment.

EXPERIMENTAL TECHNIQUES

Glass samples were prepared by melting high purity sand with the carbonates of lithium, potassium, and calcium in platinum crucibles. Quenched samples were prepared by cooling droplets of the melt between metal blocks, and a number of somewhat more slowly cooled samples were made by cooling several ml of the melt directly in water. A number of slowly cooled samples were also prepared by allowing the melt to cool for 2 h in the oven to a temperature of 1000°C. Specimens containing a total alkali content lower than 15 mole % required the use of a high frequency oven and crucibles of boron nitride. To prepare quenched samples of this composition small drops were melted on a block of graphite with the aid of an oxyhydrogen torch, the molten drops then being quickly transferred to, and pressed between metal blocks. All samples containing less than 15 mole % Li_2O were ground and pressed into pellets in order to improve the filling factor. Spectra were recorded with a Varian-4250 wide line spectrometer, equipped with a Fieldial and stabilized at 16 000 Mc/s by the clock frequency from a digital counter. The magnetic scan was calibrated using the normal sideband technique. The stability and the reproducibility of the magnetic scan was so high that all spectra recorded during the course of the investigation could be compared directly. The results of the measurements are shown in Figs. 1–8. For the sake of clarity the spectral lines submitted are reproduced by smooth lines giving an approximate mean value function from which superimposed noise has been averaged out. The background noise is reproduced only for the samples of the lowest alkali content (Fig. 1). Samples of a Li_2O content greater than

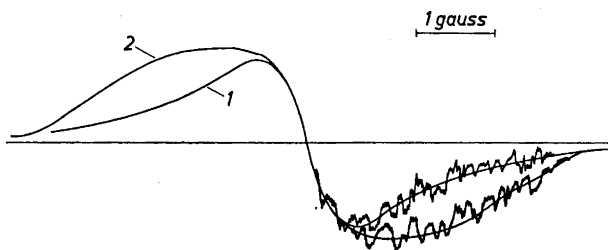


Fig. 1. The ^7Li -resonance of a lithium silicate glass containing 6 mole % Li_2O and 94 mole % SiO_2 .

1. Sample prepared by quenching from the melt;
2. Sample prepared by slow cooling of the melt.

18 mole % displayed spectra with a very low noise level. As the samples had different filling factors the intensity scale was arbitrary, and the intensities could not therefore be compared between the different spectra, nor between those reproduced in the same diagram. We have at present only compared the spectral shapes visually. Analytical methods for spectral shape characterization seem to be valuable in this case, but the application of such methods will be postponed awaiting the possibility of improving the signal to noise ratio of spectra of the samples of the lowest contents of lithium by repeated sampling.

In order to investigate the cause of the line broadening, spectra of the samples with the highest lithium content were registered under varying conditions. By using a large high frequency field and a modulation field to give maximum signal intensity, and consequently a pronounced distortion of the line, very weak satellite lines could be seen beside the very intense central transition. These lines have previously been observed in the ^7Li -resonance of a number of Li-containing salts and glasses.¹⁻³ No second order quadrupole effects could be observed for the central transition line, which was quite symmetrical and of a shape which did not vary with the frequency of the h.f. field.

RESULTS AND DISCUSSION

The peculiar S-shape of the $\text{Li}_2\text{O}-\text{SiO}_2$ liquidus curve was early interpreted as indicating a non-uniform distribution of cations in the glass. Later work showed that the deviation from the ideal melting point depression curve decreased as the radius of the cation increased, and it was consequently concluded that the tendency towards immiscibility diminished rapidly with an increase in the cation radius.⁴⁻⁶ A non-uniform distribution of cations is also to be expected in the $\text{Na}_2\text{O}-\text{SiO}_2$ system, but the potassium, rubidium, and cesium silicates seem to approach a state in which pairs of cations are distributed randomly in the silica network. An indication as to the non-uniform distribution of cations in the melt was also obtained previously.⁷ The viscosity *vs.* composition curve for the $\text{Na}_2\text{O}-\text{SiO}_2$ system, which falls off with increasing alkali content, shows a break at about 15 mole % Na_2O , which was interpreted as being due to a considerable change in the structure at this composition. It was at that time concluded that the Na-ions are evenly distributed as pairs over the melt in the low alkali region and that the ions form micelles of higher than average alkalinity in the high alkali range. Later measurements on the lithium and sodium silicate glasses have shown that many other physical properties also exhibit a similar kind of dependence on alkali content, with a break at about 15 to 17 mole % alkali oxide. Of special importance in this respect are the measurements on the lithium and sodium silicate systems of the d.c. electric conductivity and the electric loss.^{8,9} These measurements show a very pronounced dependence on the heat treatment of the samples in the low alkali region, quenched samples being supposed to have a structure approaching that of the melt, with most of the cations evenly distributed over the network, and annealed samples a structure in which the ions are grouped in clusters.

The reason for the occurrence of a non-uniform distribution of cations has been explained in terms of the large screening demand for cations of small radius and large field strength. It is generally accepted that the silicate glasses of the alkali and alkaline earth metals show a greater stability the smaller the field strength of the cations. This phenomenon has been explained as being due to the fact that the cations of low field strength do not require precise coordination conditions as far as the surrounding oxygen atoms are concerned, so that a considerable degree of disorder, characteristic of the glassy state, would be expected in systems containing these cations. It is also a well-known fact that the coordination conditions of cesium and oxygen vary considerably for cesium atoms occupying different crystallographic sites in the crystals of cesium salts, whereas this is not the case in the corresponding crystals of lithium and sodium. It should thus be assumed that the cationic clusters in glasses containing cations of high field strength form regions of a rather high degree of order, with respect to both coordination conditions and composition, these properties thus approaching those of stable crystalline compounds.

PURE LITHIUM SILICATE GLASSES

The spectra of the pure lithium silicate glasses of the low as well as the high alkali range are shown in Figs. 1–4. These spectra display a line shape which is heavily dependent upon composition and heat treatment of the samples. The spectra of the quenched samples of the low alkali range contain at room temperature a dominating narrow component line and a weaker broad component. The actual spectral shape of a sample of 12 mole % Li_2O is shown in Fig. 2 and a spectrum of similar type is obtained for a sample of 9 mole %

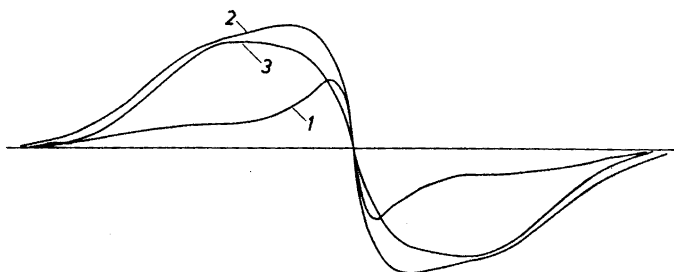


Fig. 2. The ^7Li -resonance of a lithium silicate glass containing 12 mole % Li_2O and 88 mole % SiO_2 . 1. Sample prepared by quenching from the melt; 2. Sample prepared by rapid cooling of the melt in water; 3. Sample prepared by slow cooling of the melt.

Li_2O . However, for the sample of the lowest alkali content of only 6 mole % Li_2O only one spectral line of intermediate width is observed (Fig. 1). It seems probable that the chilling of this sample has been less effective, due to the higher viscosity of this particular glass. A pronounced rearrangement of the cations could therefore be assumed to occur during the chilling procedure used for these glasses, which is why the cation distribution of the glasses of higher alkali content could be assumed to resemble more closely that of the melt. As a further consequence of the slower cooling, pellets of about 50 % higher thickness are obtained from the glass containing only 6 mole % Li_2O , than from the other glasses of higher alkali content. The spectra of the slowly cooled samples of these glasses contain a dominating broad component line. The presence of a narrow component very poorly resolved from the broad line could possibly be observed in the spectrum of the glass containing 12 mole % Li_2O . The high noise level does not allow us to distinguish such fine structure details in the spectra of the other slowly cooled samples of lower alkali content.

The spectral shape is practically independent of cooling rate for the samples of the high alkali range. The spectra also display very similar shape for samples within the whole composition range from 18 to 40 mole % Li_2O at room temperature. One broad component line of high intensity is observed here, besides a narrow line only poorly resolved from the broad one (Fig. 3). These different lines of varying width are probably to be attributed to lithium ions with different degrees of thermal motion. On cooling the samples below

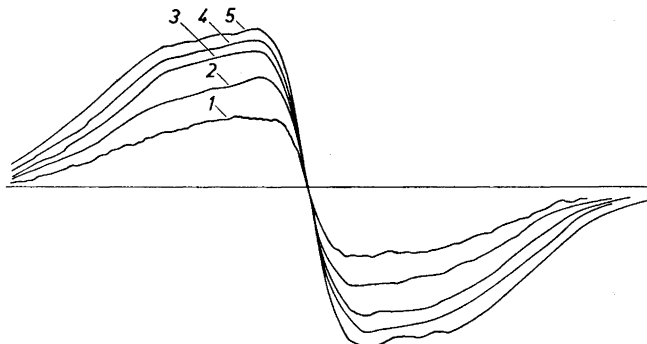


Fig. 3. The ${}^7\text{Li}$ -resonance of lithium silicate glasses of the high alkali range.

1.	Sample containing 18 mole % Li_2O and 82 mole % SiO_2 ;
2.	24 76;
3.	30 70;
4.	33 1/3 66 2/3;
5.	40 60.

—100°C the spectra of all glasses display only one broad component line of a width roughly 10 % broader than the width of the broad line registered at room temperature. At this low temperature the line width appears to be the same for all samples of the high alkali range with a content of alkali oxide between 18 and 30 mole %. For the samples of the highest contents of alkali, that is, samples in the range 33½ to 40 % alkali oxide, the line width appears to be somewhat larger and very close to the width of the crystalline lithium silicate samples, Fig. 4. For the quenched samples the line width

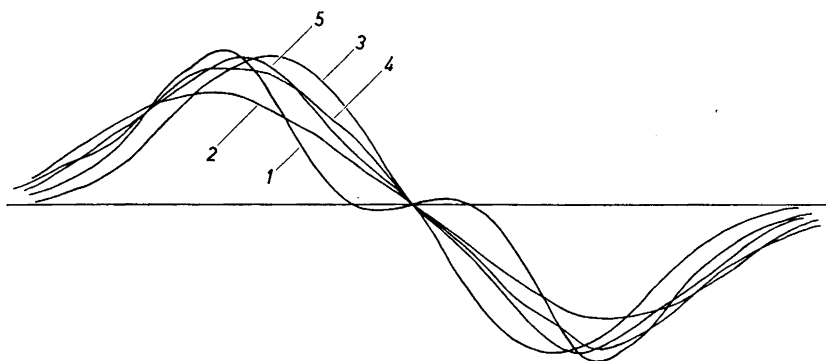


Fig. 4. The ${}^7\text{Li}$ -resonance of some samples at low temperature where no motional narrowing effects the spectral shape.

1. Crystalline lithium disilicate ($\text{Li}_2\text{O} \cdot 2\text{SiO}_2$) at -160°C and room temp;
2. Crystalline lithium metasilicate ($\text{Li}_2\text{O} \cdot \text{SiO}_2$) at -160°C and room temp;
3. Pure lithium silicate glass of 30 mole % Li_2O at -160°C ;
4. Pure lithium silicate glass of 33 1/3 mole % Li_2O at -160°C ;
5. Pure lithium silicate glass of 40 mole % Li_2O at -160°C .

seems to be somewhat smaller, the second moment of the lines being about half the value for the other samples. As the line broadening at this low temperature is dependent mainly upon the dipolar coupling, important information regarding the distribution of cations in the glass could also be extracted from such data. The significant information here is, however, to be taken from the samples of the lowest alkali content. Such investigations are at present very uncertain due to the low signal strength obtained from these samples.

Spectra have also been registered for all glass samples with narrow temperature steps from room temperature to $+230^{\circ}\text{C}$. Both line components of the spectra are rapidly narrowed on increase of the temperature above room temperature. The presence of two component lines could be observed in the spectra of glasses in the high alkali range only for temperatures up to $+50^{\circ}\text{C}$. The line narrowing effect here is to be attributed to the diffusional movement of the lithium ions. The jumping frequency, and with this the activation energy, could in this case be determined from the temperature dependence of the line narrowing according to the theory of Bloembergen, Purcell and Pound.¹⁰ This theory was originally developed for the relaxation phenomenon in liquids, but it has also found wide application to solids where rapid reorientation of resonant nuclei takes place.

The NMR spectra of the lithium disilicate ($\text{Li}_2\text{O}\cdot 2\text{SiO}_2$) and the metasilicate ($\text{Li}_2\text{O}\cdot\text{SiO}_2$) crystals have also been registered (Fig. 4). These spectra display one broad line of a width which is close to the line width for the glasses at low temperature. The metasilicate crystal gives a quite smooth spectral line, whereas the spectrum of the disilicate crystal has a rather uncommon shape which probably should be interpreted in terms of a poorly resolved fine structure of the spectral line. The spectrum has a very low signal intensity in a large interval around the resonance centre, a feature that makes it easy to distinguish from the spectra of the glasses at room temperature.

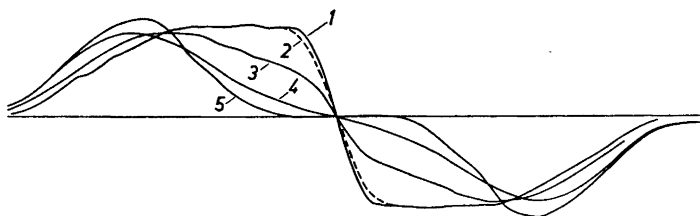


Fig. 5. Crystallization of a lithium silicate glass of 20 mole % Li_2O and 80 mole % SiO_2 . The ^7Li -resonance for heat-treated samples.

1. Sample prepared by quenching from the melt;
2. Further heat treatment at 650°C for 1.0 h;
3. Heat treatment at 650°C for 3.5 h;
4. » » » 650°C » 5.0 h;
5. » » » 650°C » 10.0 h.

A number of spectra of glasses which were given different degrees of heat treatment into complete crystallization have also been registered at room temperature (Fig. 5). A glass containing 20 mole % Li_2O was used in the

investigation. The degree of crystallization for heat treated samples of this composition has previously been determined by X-ray diffraction.¹¹ The intensity of the narrow spectral line began to decrease after about 2 h of heat treatment at 650°C of the quenched sample, and a spectrum indicating complete crystallization was obtained after 5 h. These time limits are in fair agreement with those obtained in the earlier crystallization experiments. The results, although rather qualitative, seem to show that during the crystallization process lithium ions contributing to the narrow component line are transferred into other positions where they have a much higher activation energy. They seem also to show that stable glasses in the high alkali range which do not include lithium ions contributing to the narrow component line cannot be prepared.

A number of glasses covering the whole of the high alkali range were prepared by very slow cooling, the temperature being decreased from the transformation temperature to room temperature over a period of three hours. Vitreous samples were produced in the whole of the composition range, those with an alkali content between 18 and 24 mole % being highly turbid. The spectra of these samples resemble those of the corresponding quenched samples, and only a very slight decrease in the intensity of the narrow component line could be detected. The state of the lithium ions contributing to the narrow line is thus not changed in the first stage of the heat treatment, during which the structure of the glass is altered from a state where the immiscible phases form irregular regions of small extension to a structure where the alkali-rich phase forms large spherical droplets.

INTERPRETATION AND COMPARISON WITH EARLIER RESULTS

The motional narrowing effect of the narrow and broad components seems to be reproduced reasonably well by the BPP equation. By a direct application of this equation the activation energies are obtained as 0.10 and 0.20 eV, respectively. These values appear surprisingly low compared with activation energies determined from d.c. conductivity and dielectric loss measurements on this system.⁸ A value for the activation energy of about 0.62 eV is obtained from the d.c. conductivity as well as from the dielectric loss measurements for the glasses of the high alkali range. This energy is attributed to a diffusional motion of lithium ions within alkali-rich regions or clusters of cations in the glass. As the activation energies coincide well for the two different types of measurements, it is supposed that the regions of higher than average alkali content form continuous structures throughout the whole of the glass body. The migrational motion of cations through these regions is then supposed to be responsible also for the d.c. conductivity through these glasses. For the investigated annealed glass samples of the low alkali range the activation energy is obtained as 0.68 eV from the dielectric loss measurements, whereas the d.c. conductivity loss measurements give a value as high as 1.30 eV. The former energy is also here attributed to a migrational motion of cations within alkali-rich regions whereas the latter energy is supposed to be associated with a diffusion process of the cations through a continuous silica-rich phase. This phase, which is supposed to enclose the alkali-rich regions, probably has a

structure very close to that of pure silica glass. A very high activation energy is then also to be expected for the diffusion of cations through the hard matrix. For the quenched samples of the same glass composition the activation energies are obtained as 0.78 and 1.09 eV, respectively.

There may exist the possibility that activation energies of different types of movement are being measured by the different methods. This must obviously be the case as concerns the d.c. conductivity and the dielectric loss measurements of the quenched glasses. A similar discrepancy between activation energies determined by NMR and electric measurements would point to the presence of a motional mechanism which does not result in an overall material transport or in a net polarization. Charles has discussed some different possibilities of that kind¹² regarding the migration of defects, but concludes from the similarity of the activation energies from the d.c. conductivity and the dielectric loss measurements that the phenomena involved here are closely related. Because of this similarity, which has also been demonstrated to hold true in a large number of high alkali silicate glasses,¹³ the possibility of a distribution of potential energy barriers has also been ruled out. Such a concept was introduced previously in order to explain the presence of a distribution of relaxation times. Later work¹⁴ has shown also that the shape of the dielectric absorption curves is independent of temperature, which condition indicates that the spread in the activation energies must be small, and that the large width of the loss curves could be explained by the assumption of a spread in the values of the vibration frequencies. Considering these facts it seems advisable also to pay attention to the possibility that the discrepancies could be due to large uncertainties in the methods of evaluation. A large number of different causes have to be considered in this respect as far as the NMR measurements are concerned.

The BPP equation is derived under the assumption of a rapid nuclear motion, which will result in an absorption spectrum approaching the Lorentzian shape. This condition seems to be reasonably well fulfilled at high temperatures, but it is obviously not so over the whole of the temperature range where a motional narrowing effect is observed. The shape of the broad component is namely changed considerably in the low temperature interval. The rigid lattice line shape diverges very much from the Lorentzian. This spectrum shows signs of a fine structure, which resembles that of the spectrum of the lithium disilicate crystal. Owing to the method of evaluation, there are also uncertainties for the high temperature interval. The BPP equation states that the line width should approach zero at high temperatures. This is generally not the case for solids, and an *ad hoc* modification of the equation where a correction is introduced for this remaining broadening¹⁰ may then be used. The line width decreases rapidly for temperatures up to 150°C but remains constant for a further increase of temperature to 230°C. The modified versions have been employed in the high temperature interval, where the correction is of significant importance.

The effect of the satellites has also to be considered here. The maxima of the satellites are, for the rigid lattice, well resolved from the central line. When the sample is heated, the separation between the satellites decreases at the same time as the line width of the central line decreases. At higher

temperatures, however, the satellite maxima could no longer be resolved from the central line, and it must be supposed that in this case the satellites affect the line width of the registered spectrum. This condition is probably also reflected in the fact that the integrated area of the absorption line of the registered central transition grows quite significantly with temperature. If an extra broadening results at high temperatures due to this phenomenon, activation energies will be obtained with underestimated values. It would be of great value to investigate these conditions further by other independent methods. Activation energy determinations from relaxation measurements by spin echo would perhaps prove to be useful for the systems considered here, as well as for the lithium borate glasses, where previous NMR measurements have also revealed activation energies which are much lower than those obtained from d. c. conductivity measurements.¹⁵

Irrespective of how the discrepancy between the activation energies as determined from the electric and the NMR measurements may be explained from future measurements, we can conclude that the broad line and the activation energy associated with this line are to be attributed to the movement of lithium ions within the alkali-rich clusters. This conclusion could be drawn as the broad line is the one that dominates heavily in the heat treated low alkali glasses, where the electric measurements have shown that the major part of the alkali ions are present in clusters. The most interesting result of the measurements on the lithium silicate system is that the narrow line dominates in the quenched low alkali glasses and that the corresponding activation energies are much smaller than those determined from the conductivity and the loss measurements.

To explain the motional narrowing effect in the quenched glasses in the low alkali range we have to presume the existence of one more motional mechanism for the lithium ions, which probably does not result in any overall material transport through the glass. A structural model of the distribution of cations in the alkali silicate glasses has recently been obtained from the study of the phase diagrams of these two component systems.⁶ It seems possible to explain the existence of the very low activation energy for the narrow component line from this structural model. It has been shown namely that the number of cations in the clusters could be related to the slope of the liquidus curve close to 100 mole% silica for the binary alkali silicate systems of low alkali content. The analyses of the phase diagrams indicate that lithium forms clusters containing six ions, sodium four ions and potassium and heavier alkali metals two ions in the melt. At higher alkali content the clusters are supposed to interconnect and to form continuous structures throughout the silica network. The comparatively large rigid lattice line width of the NMR spectra of the quenched low alkali silicate glasses seems also to reveal that ion pairs could not be present here.

We will assume that at least some of the lithium ions of the quenched glasses of the low alkali range occupy positions which resemble the positions of the cations in the melt. Having accepted the structural model obtained from the analyses of the phase diagrams, one can assume that the narrow line of the quenched glasses has to be attributed to lithium atoms contained in small clusters of only six ions. In the low alkali glasses these clusters may be

regarded as forming a void in a hard silica-like matrix. The lithium ions have here a coordination to surrounding oxygen atoms different from that normal for ions in other positions in glasses and crystalline substances; and it may be assumed that the positive charge of the lithium ions of these small clusters is less effectively screened by surrounding oxygen atoms. This fact may explain the occurrence of the very low activation energy for a diffusional movement of the cations within the region of the cluster. It is, therefore, reasonable to lay stress upon the assumption of a thermal movement of the cations within restricted areas for the cations contributing to the narrow line.

The very open structure of the silica matrix is also of great importance in this respect. This character of the pure silica glass is clearly demonstrated by a comparison with the structure of cristobalite, which crystal has a density somewhat higher than that of silica glass. The crystal structure of α -carnegite,¹⁶ stable above 1248°C, also illustrates clearly the open character of the silicon-oxygen network. The crystal has a cristobalite-like lattice in which AlO_4 and SiO_4 tetrahedra alternate, and the sodium ions occupy some of the empty cavities in this lattice. The sodium ion is here surrounded by twelve oxygen ions and is situated in an unusually large cavity. The crystal undergoes an inversion at lower temperatures to a β -modification where aluminium has six-fold coordination and sodium a normal coordination to oxygen. The structure of the quenched lithium silicate glass can not, of course, contain structural units quite like those of α -carnegite. In spite of the presence of non-bridging oxygen atoms in the lithium silicate glass similar cavities may, however, exist here and it is a reasonable hypothesis also that the low activation energy of the narrow component line is due to a movement of the lithium ions between alternative sites of such cavities. Such a type of movement of lithium ions has been observed in a large number of crystals where the lithium ions are introduced in small amounts as impurities substituting cations of larger radius.¹⁷ It may alternatively be supposed that the low activation energy is to be attributed to a movement of lithium ions from one cavity of this type to a neighbouring one. An open structure of the small clusters of the quenched low alkali glasses should then also be assumed, which seems to be in agreement with the packing model proposed by Urns¹⁸ to explain the tighter packing obtained by formation of larger clusters.

The very open structure of vitreous silica is also clearly demonstrated from a consideration of densities. If one considers only the density of the silica glass and the sizes of the silica and oxygen atoms, the average diameter of the cavities between the SiO_4 -tetrahedra are estimated to 2.4 Å.¹⁹ From the density values of alkali silicate glasses of 20 mole % alkali oxide it is also shown that more than 100 % of the Li-ions, 70 % of the Na-ions, and 27 % of the K-ions are accommodated in holes of the silica matrix, and do not contribute to the volume. It is interesting to note that the large cavities are assumed to be present in the silica-rich parts of the glass even if cations are not included in the voids. Similar structural units are observed in crystals for high temperature modifications only.

It has to be stressed also that the assumption that all foreign entities added to silica in limited amounts are accommodated in void spaces in an undistorted silica matrix forms the essential idea for the analyses of the

slopes of the liquidus curves of binary metal silicate glasses.⁶ Such a segregation of different compounds into microphases is assumed to be characteristic for silica melts containing cations of medium field strength. We have then also to assume that the lithium ions occupy other positions in the larger clusters of the heat treated glasses and the glasses of the high alkali range. The alkali-rich regions of these glasses are probably surrounded by, and might even partly include, a silica skeleton which is heavily distorted from the structure of pure silica. The lithium ions may here obtain a normal number of surrounding oxygen atoms, which implies the formation of a tighter structure and gives rise to a higher activation energy for the diffusion of the cations within the clusters.

The infrared reflection spectra of the alkali silicate glasses²⁰⁻²⁶ may be interpreted as giving independent support for these conclusions. The spectral band of pure silica glass in the range due to the stretching vibration exhibits an intense narrow line, which is quite close to the spectral line of cristobalite. On the addition of alkali the spectral line is broadened and displaced to lower wave numbers, the change proceeding continuously with increasing alkali content in the potassium silicate system, though more discontinuously in the lithium silicate system. The highly ordered structure of pure silica glass is obviously changed to a less ordered structure by the addition of alkali. The introduction of even small amounts of potassium, distributed randomly over the structure, may be assumed to affect the binding forces of a considerable part of the network, whereas the formation of cation clusters in the lithium silicate system implies that a considerable part of the silica still exists in a structure close to that of pure silica glass, even for samples with a comparatively high alkali content. A narrow component line that could be assigned to undistorted silica could be distinguished, apart from a broader line, for samples with a total alkali content up to 16 mole %. At a somewhat higher alkalinity of the samples, the infrared spectra indicate a distortion of the whole of the silica network, which is why even another type of coordination of the cations could reasonably be assumed here.

In the spectra of the glasses of the high alkali range one narrow component line is observed in addition to the dominating broad line. The activation energies associated with this line are only somewhat higher than the energies determined from the spectra of the quenched glasses of the low alkali range. Some of the lithium ions of the high alkali glasses thus seem to be in positions resembling those of the cations of the quenched glasses. A total structural similarity between these two types of cations could not, however, exist for several reasons. We will assume that the similarity concerns a motion of lithium ions between alternative sites within a void. The fact that the d.c. conductivity is very well described by only a single exponential term over a rather large temperature interval⁸ seems also to verify that the thermal motion associated with this lower activation energy does not contribute to the overall material transport. The lithium ions giving rise to the narrow component lines of the low and high alkali glasses behave very differently in one respect. The intensity of the narrow line is reduced very quickly upon heat treatment of the low alkali glasses, whereas for the high alkali glasses this same line is very little affected unless the heat treatment is prolonged to

partial crystallization. Lithium ions occupying positions in voids of the high alkali glasses thus seem to exist in a state of much higher stability than the corresponding ions in the low alkali glasses.

The results of the recent investigations of the lithium silicate system with the aid of an electron microscope²⁷⁻³³ have also to be considered in relation to the results discussed above. It is shown that liquid immiscibility exists in all lithium silicate glasses other than those of the disilicate composition, and for this reason it has been assumed that one of the phases of the glasses approaches this composition. Even for the quenched low alkali glasses a phase segregation is observed⁸ where one irregular and tubular phase of comparatively small droplets is distributed in a continuous phase which probably has a lower alkali content. A quite homogeneous distribution of cations or small clusters of cations is thus not to be expected in the quenched glasses. Furthermore, it has been shown that in the slowly cooled samples one phase accumulates as droplets in another continuous phase and that the diameter of the droplets has a maximum value at an alkali concentration somewhere between 15 and 20 mole % alkali oxide. The size of the droplets is assumed to depend on the composition. It may then be supposed that the lithium ions accumulate mainly as clusters in the droplet phase for samples in the low alkali range and that the alkalinity of this phase increases continuously with the overall alkalinity of the sample, whereas the continuous phase consists of nearly pure silica. At a total alkali content somewhere between 15 and 20 mole % the droplet phase has been supposed to reach the disilicate composition, and it has been assumed that the composition of this phase remains constant, while the alkali content of the continuous phase increases further with increasing total amount of alkali in the system. The rigid lattice line width of the NMR measurements, on the other hand, shows that a pronounced structural difference exists between glasses in the composition range of 18 to 30 mole % alkali oxide and the glass of the disilicate composition. A content of alkali oxide somewhat below the disilicate composition is thus to be supposed for the droplet phase.

We regard it as a very interesting result of the NMR measurements that the characteristic spectral pattern, shown in Fig. 3, is observed at room temperature also for a glass of the disilicate composition. This means that the NMR spectra indicate the presence of lithium ions in two different positions in a glass where only one phase is observed. It could therefore also be assumed that the lithium ions are present in these two positions in the droplet phase of all high alkali glasses. It seems reasonable here to put forward the assumption that the two different cation positions are to be attributed to different microstructures of the glass. The low activation energy observed for the NMR measurements of the narrow line of the high alkali glasses should then also be associated with a movement of the cations between alternative sites within a cavity. It seems most acceptable to assume that such cavities are formed within the silica skeleton, and we will for this reason also assume that lithium ions contributing to the narrow component line are included in the silica-rich microphase. This implies that a number of silicon-oxygen bridges of the silica skeleton are broken and that the skeleton here is less firmly bonded together. When adopting this model, our crystallization experiments

may be interpreted to show that lithium ions are transferred from the silica-rich regions to the lithium-rich microphase during the crystallization process. This implies a rearrangement of the silica skeleton to a more ordered structure, which process might perhaps even be rate-limiting for the crystallization.

The assumption of micro-heterogeneities in the high alkali glasses seems to be strongly supported by a comparison with the structure of the corresponding crystalline silicates. A segregation into different microphases is here more pronounced in crystals of a low content of alkali ions. Heterogeneous regions could thus be distinguished in crystals of the disilicate composition, where silicate sheets are present. They are less pronounced in the metasilicate crystals where silicate chains are formed. It is interesting to observe here that stable glasses of the disilicate composition could be prepared easily, whereas glasses of the metasilicate composition cannot be produced. The structures of the α and β forms of the lithium and the sodium disilicate crystals have been determined accurately.³⁴⁻³⁶ These crystals contain silicate sheets and cations also arranged in sheets. As a consequence of the heterogeneous structure the cations have here a small and well-defined number of near-neighbour cations. The observed splitting in the NMR spectrum of the lithium disilicate crystal probably reflects this condition. The spectrum has a very low intensity in a large interval around the resonance centre in the observed derivative of the absorption line. Spectra of a similar type are known to result in powder patterns of substances containing demarcated groups of resonant nuclei. Such conditions are observed, for example, for the ^1H -resonance of the rigid NH_4 -group. The metasilicate crystals of both lithium and sodium contain simple linear silicon-oxygen chains.³⁷⁻³⁹ The segregation between the microphases is not so clearly pronounced in these crystals, each ion being surrounded by seven nearest neighbours. The Li-containing crystal also displays an even NMR spectrum, in accordance with this description. The pure lithium silicate glasses display also at low temperatures spectra which resemble more closely that of the disilicate crystal, which thus gives an indication of a microphase separation also in the glass.

LITHIUM SILICATE GLASSES WITH ADDITIONS OF OTHER ALKALI AND ALKALINE-EARTH IONS

The spectra of the pure lithium silicate glasses in the high alkali range exhibit at room temperature a narrow component line, which gives the spectra a very characteristic shape. This line is completely eliminated by a substitution on a molar basis of 10 % of potassium as well as magnesium, calcium, and barium for the lithium ions. The narrow line again becomes visible in the spectra of these three component glasses when registered at elevated temperatures. On the substitution of 20 % of the lithium ions the behaviour is similar, but here the narrow lines first become visible at still higher temperatures. On a still higher degree of substitution, 30 % or higher, the narrow line could no longer be detected at any temperature. These effects are demonstrated from the spectra of Figs. 6-8 for glasses of a total content of 70 mole % SiO_2 . Similar series of spectra have been registered also for glasses of a total content of SiO_2 of 76, 60, and 50 mole %.

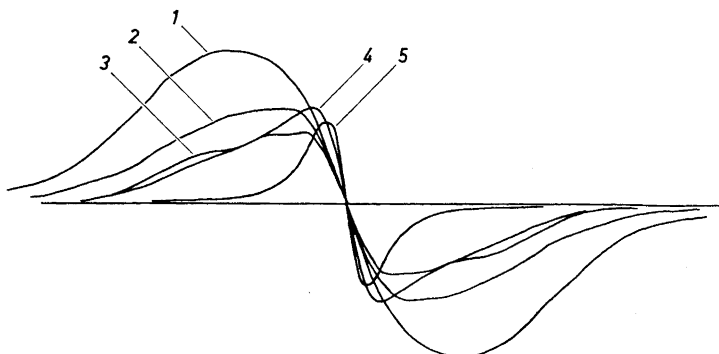


Fig. 6. The ${}^7\text{Li}$ -resonance of a lithium-calcium-silicate glass containing 22.5 mole % Li_2O , 7.5 mole % CaO and 70 mole % SiO_2 at 1. 22.0°C; 2. 50.7°C; 3. 77.0°C; 4. 87.5°C; 5. 146.0°C.

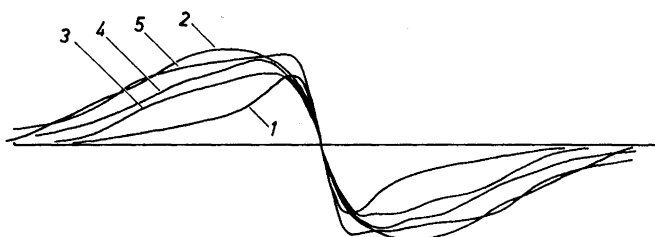


Fig. 7. The ${}^7\text{Li}$ -resonance of some three-component glasses at +77.0°C.

1. 30 mole % Li_2O , 70 mole % SiO_2 ;
2. 22.5 mole % Li_2O , 7.5 mole % K_2O , 70 mole % SiO_2 ;
3. 22.5 mole % Li_2O , 7.5 mole % BaO , 70 mole % SiO_2 ;
4. 22.5 mole % Li_2O , 7.5 mole % CaO , 70 mole % SiO_2 ;
5. 22.5 mole % Li_2O , 7.5 mole % MgO , 70 mole % SiO_2 .

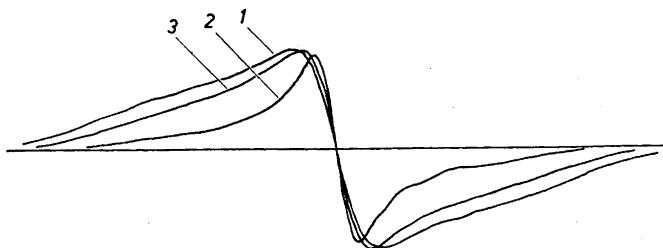


Fig. 8. The ${}^7\text{Li}$ -resonance of some three-component glasses at 97.0°C.

1. 37.5 mole % Li_2O , 12.5 mole % K_2O , 70 mole % SiO_2 ;
2. 37.5 mole % Li_2O , 12.5 mole % BaO , 70 mole % SiO_2 ;
3. 37.5 mole % Li_2O , 12.5 mole % CaO , 70 mole % SiO_2 .

second moment of the narrow line from the $p-p$ distance the activation energies are obtained as 0.25 eV at a substitution of 10 % of the lithium ions and as 0.30 eV at a substitution of 20 %. The activation energies do not depend very much upon the total alkali content within the whole of the high alkali range. For glasses of a total alkali content from 20 to 30 % the activation energies seem to depend somewhat upon the nature of the substituent. Variations in the activation energies of ± 5 % around the mean value can significantly be determined from the spectra. Substitution with Mg gives the lowest value of the activation energy and the size of this quantity grows in the order Ca, Ba, and K. The effect thus seems to be related to the field strength of the substituting ion. For glasses of a total alkali content of 35 to 50 mole % no variations in the values of the activation energies with the nature of the substituting ions could be detected.

The broad component line of the spectra is affected very much by substitutions of other ions for lithium. The motional narrowing effect develops at higher temperatures in all of the three component glasses than in the pure lithium-silicate glasses. The activation energy for the diffusion of lithium ions within the large clusters also increases appreciably upon these substitutions. For glasses of a total alkali content of 20 to 40 mole % the activation energies are, to some degree, dependent upon the nature of the substituent. The increase of the activation energy is thus largest on the addition of potassium and only somewhat smaller on the addition of the alkali-earth ions. The situation is somewhat different for the glasses of the highest alkali content with a total amount of alkali of 50 mole %. When barium is substituted for lithium the broad line is narrowed with increasing temperature much more rapidly, than when other ions are used for the substitution. The data obtained regarding the activation energy are thus rather easily summarized for three component glasses in the composition range of 50 to 80 mole % silica and with a lithium content higher than 12 mole %. Activation energies have been determined for mixed glasses with a content of 70 mole % SiO_2 . By substitution of 10 % of the lithium ions the activation energy is obtained as 0.28 eV and by a substitution of 20 % as 0.34 eV. For higher degrees of substitution the activation energies are obtained with a lower accuracy. They seem to approach a value around 0.4 eV for glasses with between 40 and 60 % of the lithium ions substituted. Glasses of a still lower lithium content exhibit other interesting features. For samples containing only 6 mole % lithium and between 50 and 70 mole % silica and the remaining part potassium, a motional narrowing effect in the spectra is first observed at temperatures above $+150^\circ\text{C}$. Quenched glasses of similar composition but with calcium as the substituent exhibit a spectrum at room temperature containing a dominating narrow line. The activation energy determined from this line is in the region of 0.12 eV. After heat treatment of the samples for some hours at 650°C , only one broad line is observed in the spectra at room temperature. The properties of these samples thus very much resemble the pure lithium silicate glasses of the low alkali range.

INTERPRETATION AND COMPARISON WITH EARLIER RESULTS

The change of the activation energy of the broad line with the degree of substitution follows earlier experience closely. This activation energy is supposed to be associated with the diffusion of lithium ions in the large clusters. A number of different causes have been given to explain the physical properties of glasses containing mixtures of alkali ions or alkali and alkaline-earth ions.

The variations observed in the activation energies of the broad component line of the lithium potassium silicate glasses should obviously be assigned to the mixed alkali effect. A large number of physical properties for the mixed alkali silicate glasses are, in a similar manner, not linearly dependent upon the composition. Electric conductivity, density, elastic moduli and hardness all show deviations from linearity which indicates a firmer binding between the alkali ions and the silica matrix for the mixed glasses than for the pure two component systems. To account for the increase in the activation energy for the diffusion of lithium ions with the increased addition of potassium to the glass the most simple interpretation of the mixed alkali effect can be made. According to this theory more polarizable non-bridging oxygen atoms are introduced in the glass with the potassium ions. These atoms are assumed to give a stronger bond to the lithium ions, and to produce a more efficient screening of the positive charge of the latter. This simple picture cannot, however, account for the fact that the activation energy also grows at a rather similar rate on the addition of ions of a field strength higher than that of lithium. The substitution effects when forming mixed alkali-alkaline-earth silicates resemble very much those of the mixed alkali silicates even with regard to the other physical properties mentioned. Thus other causes must also be effective and probably also dominating in determining the properties of glasses containing mixtures of cations. The blocking effect has been put forward as one possible explanation to account for the decrease of the conductivity when the cations are mixed. In a mixture where the cations are of different size the mobility is supposed to be lowered due to the fact that the ions could not enter a hole previously occupied by an ion of different size, unless this hole changes its size.¹⁸ To account for the pronounced densification observed when a mixture of alkali ions or alkali and alkaline-earth ions are introduced in a silicate glass, a more refined model seems necessary. The dynamic interpretation of the mixed alkali effect also accounts well for this phenomenon and might also satisfactorily explain the great similarity of the physical properties of glasses containing mixed alkali ions and a mixture of alkali and alkaline-earth ions.⁴⁰ According to this model it is assumed that cations of different masses repel each other to a smaller extent than ions of the same mass, according to the unharmonicity of the thermal vibration. This increases the bond strength between the cations and the oxygen atoms and leads to a tightening of the glass.

On substitution of a small amount of other ions for lithium the increase of the activation energy associated with the narrow line, is probably to be attributed to causes similar to those responsible for the changes in the size of the activation energy derived from the broad line. As there are reasons to assume that the diffusion movement, responsible for the motional narrowing effect upon the narrow component line, is restricted to cavities in the sample, it is also a reasonable assumption that the tightening of the glass on substitution is the main reason for the increase of the activation energy. The voids could be assumed to shrink as the glass is tightened on substitution of some of the lithium ions by other ions. At a degree of substitution above 30 mole % the voids may then be assumed to be so effectively tightened that a movement of lithium ions between alternative sites within the void is no longer possible.

Some earlier investigations may be referred to, which demonstrate the close similarity of the physical properties of lithium and sodium silicate glasses with additions of potassium and alkaline-earth ions. This is most clearly demonstrated by electric conductivity measurements on some lithium silicate glasses.⁴¹ Substitution of some of the lithium ions by potassium and calcium results in a pronounced decrease of the conductivity, where the values observed for glasses containing potassium are only somewhat smaller than those of glasses of similar composition containing calcium. The activation energies of the electric conduction show a similar behaviour.^{42,43} The density data reveal that a pronounced compacting results when potassium⁴⁴ or calcium^{19,45} are partly substituted for sodium. An increase of the value of the elastic moduli is also observed to follow parallel with this densification.^{44,46} On partial substitution of sodium ions for magnesium quite different results are obtained.^{19,47} No compacting of the glass is observed here, and it is supposed that magnesium in such alkali-containing glasses acts as a network former entering four-fold coordination to oxygen. In alkali-free glasses on the other hand, magnesium most efficiently densifies the glass, and it is supposed that magnesium here occupies octahedral positions. The effect on the NMR ⁷Li-resonance upon partial substitution with magnesium seems to resemble the effects observed by other methods of investigation in the alkali-free glasses. We will assume, therefore, that magnesium acts mainly as a network modifier in the mixed lithium magnesium glasses. Due to the high field strength lithium does not behave as a typical alkali ion, and it does not seem surprising that some properties of lithium-containing glasses are closely related to those of glasses mainly containing alkaline-earth ions.

The substitutional effects appear to be very different for quenched glasses of the lowest content of lithium but of a high total content of cations. The activation energies for the thermal motion of lithium are here heavily dependent upon the field strength of the substituents. The presence of a narrow component line in the spectra of glasses containing calcium with an associated very low activation energy, seems hard to explain unless a motion of lithium ions within restricted regions is presumed. The quenched calcium silicate glass may be supposed to form a hard matrix, where the structure is such that the calcium ions achieve a normal coordination whereas the lithium

ions, when present in small amounts, are placed in non-ideal positions. The conditions are obviously quite different in the mixed potassium lithium silicate glasses of a low content of lithium. Here potassium gives rise to a large number of highly polarizable non-bridging oxygen atoms which make the lithium ions more compatible with the silica skeleton.

All interpretations regarding the mixed glasses always rest on somewhat uncertain grounds since a segregation into different phases of unknown composition occurs in many of the samples. As long as mixed effects are really observed, however, the presence of pure two-component phases could be ruled out. The low activation energy observed in the mixed lithium calcium silicate glasses of low content of lithium could, therefore, alternatively, be due to the presence of a phase of pure lithium silicate, where the lithium ions occupy positions similar to those present in the quenched low alkali silicate glasses.

For glasses of the highest cation content some interesting and unexpected features appear in the NMR spectra. The line width of the broad component is here dependent upon the nature of the substituting ion in as much as glasses containing barium display spectra where the motional narrowing effect develops at somewhat lower temperatures (Fig. 8). The effect could be traced back to a lower activation energy. The phenomenon is of great interest as it seems possible to place it in relation to the extension of the glass-forming regions of the different three-component systems. The growth of the glass-forming regions of lithium silicate glass is much larger on the addition of small amounts of potassium and calcium than on the addition of barium.⁴⁸ The mixed glasses containing barium have thus a composition which is much closer to the boundary of the glass-forming region than the other glasses investigated. The lower activation energy of the barium-containing glasses then probably stands in relation to a higher crystallization rate and a more complete segregation into phases of different composition. The dynamic interpretation of the mixed alkali effect also seems to account well for this phenomenon. According to this theory, cations of different field strength should be more compatible with silica and form more stable glasses. The observed pattern is quite in accordance with this concept as the field strengths of lithium and barium are nearly the same, whereas that of calcium is much larger and that of potassium much smaller. This field seems to be a promising one for further experiments.

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