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COMPARATIVE RAMAN STUDY OF MIXED-ALKALI AND SIMILAR ION EXCHANGES--ETC(U)

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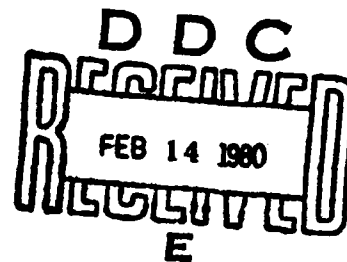
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19. ABSTRACT (Continue on reverse side if necessary and identify by block number) The Raman spectra of analogous ion exchanged and mixed alkali disilicate and aluminodisilicate glasses of the same relative composition of dissimilar cations have been determined and employed to investigate the origin of the similarity of the mechanical loss features exhibited by them. Ion exchange of Na⁺ for Li⁺ in Li₂O-Al₂O₃-2SiO₂ glasses is shown to yield glasses whose network structure is different from that of the mixed alkali glasses of the same stoichiometry, but to attain that structure upon annealing. The network structure of ion exchanged and conventionally mixed alkali disilicate glasses are apparently identical.		

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Abstract (Contd)

These results are interpreted in light of the mechanical loss spectra of the analogous glasses prepared in the two ways.

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Comparative Raman Study of Mixed-Alkali and Similar Ion-Exchanged Glasses

Introduction

The fact that key dynamic mechanical properties of ion-exchanged glasses are strikingly similar to those of mixed-alkali glasses of approximately the same overall composition (1-6) has been reported by several investigators. In particular this similarity has been observed for each of the glass systems, $x\text{Li}_2\text{O}(1-x)\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ (5) and $x\text{Li}_2\text{O}\cdot (1-x)\text{Na}_2\text{O}\cdot \text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ (6). Although evidence for it is clear, a well-developed rationale for this parallelism between the mechanical properties of conventionally "mixed alkali" and ion-exchanged glasses and experimental evidence on which to base such a rationale are lacking.

In the above-mentioned studies (5,6), the internal friction ($\tan\delta$) of mixed-alkali and analogous ion-exchanged glass fibers was determined as a function of temperature using the torsion pendulum technique at low frequency. Pertinent examples of these plots, shown in Figs. 1a through 2b, indicate the similarities. The so-called "mechanical mixed-alkali effect", as observed in the conventionally mixed alkali disilicates, is shown in Fig. 1a. As x is increased in this system ($x\text{Li}_2\text{O}\cdot (1-x)\text{Na}_2\text{O}\cdot 2\text{SiO}_2$) two effects are apparent. First, a lower temperature peak (LTP), sometimes called the "single-alkali" peak, shifts to higher temperatures and decreases in intensity; and, second, another peak, higher in temperature (HTP), often referred to as the "mixed-alkali peak", grows in and shifts to lower temperatures while increasing in intensity until x is near 0.5 ± 0.1 . At approximately this composition the HTP is at its maximum and virtually obscures the LTP peak. As x is increased further, the HTP becomes weaker and shifts back to higher temperatures, while the LTP becomes again stronger and returns to lower temperatures. As shown in Fig. 1b, a similar "mixed-alkali" effect is observed in an ion-exchanged alkali disilicate glass. At this amount of Na for Li exchange the HTP is so intense that it nearly envelopes the LTP.

Figure 1

(a) Internal friction "Spectra" of conventionally melted

 $x\text{Li}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ (gl) glasses at ($f = 0.5$ Hz)

——— 0.06 Li_2O 0.94 $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ (gl)
 ——— 0.5 $\text{Li}_2\text{O} \cdot 0.5\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ (gl)
 ----- 0.94 $\text{Li}_2\text{O} \cdot 0.06\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ (gl) (5)

(b) Internal friction "Spectra" of $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ (gl) glasses

before and after ion-exchange in LiNO_3 , KNO_3 , NaNO_3
mixture at 175°C . ($f = 5$ Hz)

----- $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ (g)
 ——— $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ (g) after ion-exchange ($\frac{1}{2}$ hr) (5)

Figure 2

(a) Internal friction "Spectra" of $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (gl)

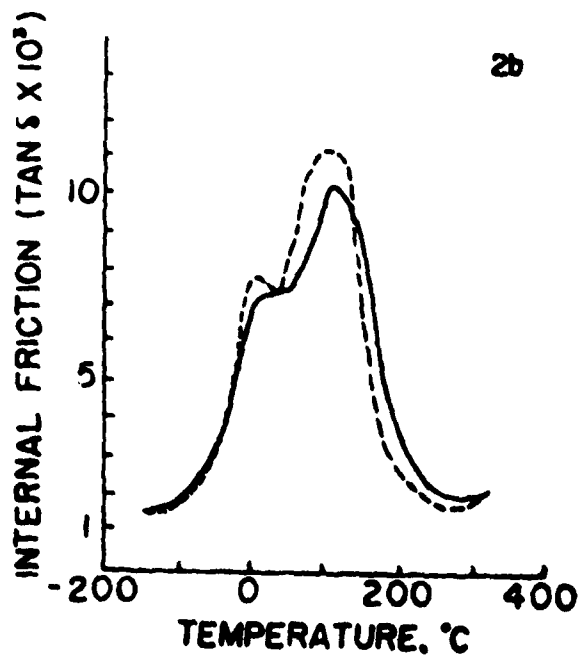
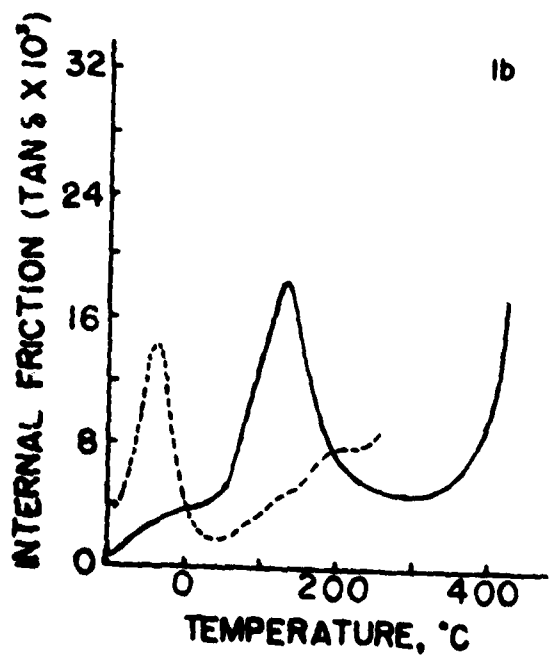
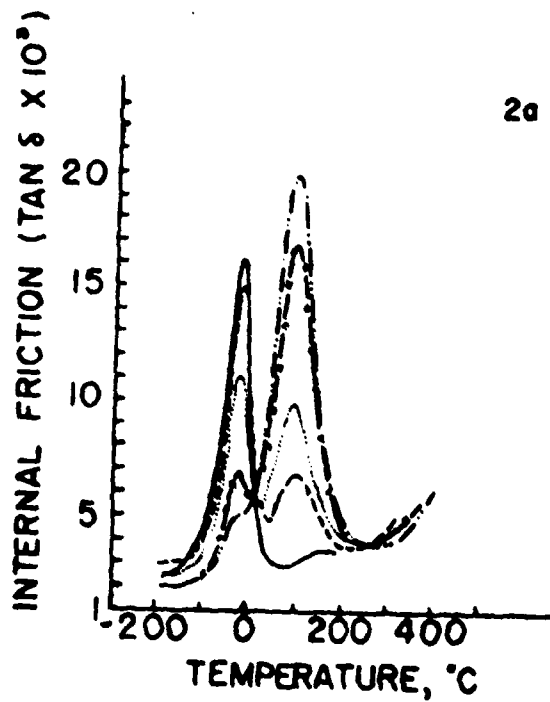
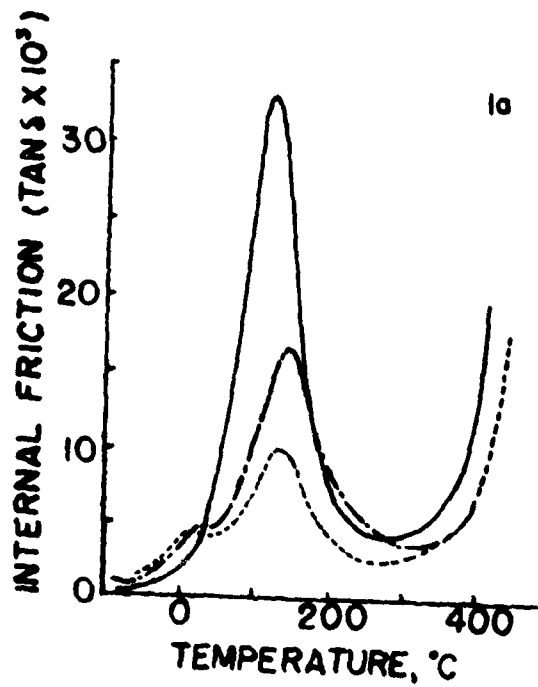
ion-exchanged in NaNO_3 at 366°C ($f = 0.5$ Hz). — 0

---- 1; 5; —x— 30; —·— 60 minutes of exchange (6)

(b) Internal friction of $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (gl) ion-exchanged

for 15 minutes in NaNO_3 at 366°C and a conventionally melted
sample of the same composition ($f = 0.6$ Hz). — ion-exchanged;

--- conventionally melted: $0.9\text{Li}_2\text{O} \cdot 0.1\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (6)



This phenomenon also is observed in ion-exchanged alkali alumino-disilicates, as can be seen in figure 2a. Again, the LTP becomes weaker as the HTP grows in and becomes quite strong at longer intervals of ion-exchange. The similarity between an ion-exchanged glass and a conventionally mixed sample of identical composition, for the alkali alumino-disilicates, is shown in Fig. 2b.

The fact that an apparent "mixed-alkali" effect is observed in ion-exchanged glasses has caused speculation as to whether these glasses are indeed "mixed", i.e. have molecular level structures that are identical (or nearly identical) to those of compositionally identical but conventionally melted "mixed-alkali" glass systems. Although there are no convincing explanations for the origins of the effects observed, there have been suggestions about why certain phenomena are not observed. Thus, Abdel-Lalif, *et al.*, attributed the failure of the HTP bands in ion-exchanged alumino-disilicates to shift in temperature to the lack of required network relaxation which is possible only at annealing temperatures (6). In the case of the alkali disilicates, de Waal, also emphasized the annealing process, and suggested that a mixed-alkali state is achievable after ion-exchange, if the glass structure is permitted to relax at an elevated temperature (5). In studies of certain other polysilicate systems (1-4, 7) similar conclusions have been reached. On the other hand, the presence of a mixed-alkali outer layer over a core of single-alkali silicate glass has been suggested as being the important characteristic in reaching a mixed-alkali-like state. Although it too must be valid under certain conditions, these conceptual approaches differ in the sequencing of the alkali diffusion-dispersion and network relaxation.

In order to address the question of whether the mixed alkali and ion exchanged glasses are as similar in structure as their mechanical properties have suggested, and of what the role of relaxation at annealing temperatures is, we have undertaken a study of the variation in molecular properties through analogous series of glasses. Our approach employs Laser-Raman spectroscopy to study these changes.

This method is based upon the assumption that if the structures found in ion-exchange and their analogous mixed-alkali glasses are the same, it should be apparent from the Raman spectra; and thus similarities in their mechanical spectra are to be expected. However, if the Raman spectra should differ significantly (due to microstructural variations or bulk heterogeneities, such as phase separation), then an explanation which is independent of these differences is required. In any event, a more profound explanation of the special mechanical behavior of mixed alkali glasses and ion-exchanged glasses is needed, and the spectra should assist in its formulation.

Experimental Procedure

Preparation of Mixed-Alkali Disilicates. Mixed-alkali glasses of the composition $x\text{Li}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ were prepared following the procedure used by de Waal (5) from appropriate amounts of reagent-grade SiO_2 (floated powder, 240 mesh), Na_2CO_3 and Li_2CO_3 . After mechanically combining the components, about 7g of the mixture was melted in a 20 ml platinum crucible at 1350°C in an open air electric furnace. Enough time was given to allow the melts to become visibly homogeneous. Bubbles of CO_2 are liberated during the reaction and tend to linger within the viscous fluid melt. But with occasional stirring (with a fused silica rod) over the heating time of 3 to 4 hours, a clear melt of each composition in the series was obtained.

Upon removal from the furnace, the melts were allowed (about 15 seconds) to become viscous enough for fibers to be drawn. Glass fibers about 0.5 mm in diameter and 15 mm long were then drawn with a fused SiO_2 rod, cooled, broken into 5 cm lengths, and stored in a dessicator over CaSO_4 .

Elemental analyses were performed on the mixed alkali disilicate fibers by Galbraith Labs, Inc., Knoxville, Tennessee. The actual alkali compositions of representative fibers (expt) compare with the melt compositions (predicted) as follows. For $0.85\text{Li}_2\text{O} \cdot 0.15\text{Na}_2\text{O} \cdot 2\text{SiO}_2$; Li(expt) 7.6% (pred.) 7.6%, Na(expt) 4.0% (pred.) 4.4%. For $0.5\text{Li}_2\text{O} \cdot 0.5\text{Na}_2\text{O} \cdot 2\text{SiO}_2$; Li(expt) 4.2% (pred.) 4.2%,

Na(expt) 13.8% (pred.) 15.3%. And, for $0.25\text{Li}_2\text{O} \cdot 0.75\text{Na}_2\text{O} \cdot 2\text{SiO}_2$; Li(expt) 2.0% (pred.) 2.0%, Na(expt) 19.8% (pred.) 19.7%. Thus, the actual compositions are quite close to the nominal ones for which the batches were prepared, and the experimental compositions are employed wherever relevant.

Preparation of Mixed-Alkali Aluminodisilicates. A similar procedure was followed in preparing mixed-glasses of the composition $x\text{Li}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$. Reagent-grade Al_2O_3 was used in addition to SiO_2 and the alkali carbonates. The mixtures were heated at 1550°C to obtain a homogeneous melt; and as for the previous system, glass fibers were drawn and stored in a dessicator.

Preparation of Ion-Exchanged Glasses. Glass fibers of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ and $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ($x = 1$) were used for the ion-exchange experiments. Following the procedure of Abdel-Latif, *et al*, (6) exactly, the fibers were cut to about 2 cm in length, immersed in a 20 ml crucible of molten NaNO_3 at 350°C for various amounts of time, and stirred periodically. After exchange, they were cooled, washed with distilled water, dried, and stored in a dessicator over CaSO_4 . To confirm that exchange had occurred and to provide a connection between exchange time and total amount of exchange elemental analysis of an ion-exchanged fiber was carried out by Galbraith Labs. It showed that the Na^+ for Li^+ ion exchange that occurred in 24 hours under these conditions yielded a fiber whose ratio of Na^+ ions to Li^+ ions was 3.05 to 1.0. This corresponds in overall stoichiometry to $0.247 \text{Li}_2\text{O} \cdot 0.753 \text{Na}_2\text{O} \cdot 2\text{SiO}_2$.

The effect of annealing on the ion-exchanged alkali aluminodisilicates was also examined. Fibers of $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (g) which had been Na-exchanged for 24 hours was heated at 590°C in an open-air electric furnace also for 24 hours, and their Raman spectra examined.

Raman Spectra. Raman spectra were obtained for all of the samples prepared using a Jarrell-Ash 25-300 Raman Spectrometer, and the 488.0 nm line of a Spectra Physics 164 Argon ion laser excitation. The fibers were oriented such that their cross sections were perpendicular to the excitation beam. Radiation scattered

at 90° was collected by the detector. The laser beam diameter was slightly greater than fiber thickness, so the spectra contain Raman Scattering from the entire fiber and any scattering elements present in the sample should contribute to the spectra.

Electron micrographs of both the alkali silicates and alkali aluminodisilicates were taken using an AMR Model 1000A Scanning Electron Microscope. Glass fibers were mounted such that their cross sections were exposed for analysis. These were polished and gold coated previous to microscope examination. At a magnification of 1000x the samples were homogeneous. Photographs at magnification 8000x show some irregularities attributable to tiny bubbles of CO₂ trapped within the glass or to stress cracks.

Spectral Results

Mixed Alkali Disilicate Spectra

The Raman Spectra of the glass system $x\text{Li}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ exhibit four prominent bands, each of which shifts in frequency as x changes. As shown in Figure 3a for $x = 0, 0.5$, and 1.0 . The most notable shift occurs for the high frequency band, which occurs at approximately 1100cm^{-1} . A summary of its behavior is presented in Fig. 5a. Changes are also observed in the broad band which occurs at approximately 575cm^{-1} , and they are presented in Fig. 6a. The small shift in frequency of this band (about 10cm^{-1}) probably is due to the effect of the change in background intensity that occurs as Li^+ is replaced by Na^+ in the mixed alkali series.

Sodium Ion-Exchanged $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ Fibers. Comparison of the bands in the Raman spectra ion-exchanged glasses with those of the conventional mixed alkali glasses shows their similarity quite clearly. The Raman spectra of $\text{Li}_2\text{O} \cdot 2\text{SiO}_2(\text{gl})$ ion-exchanged for various times in NaNO_3 (1) are shown in Fig. 3b. As is apparent from Fig. 5b the " 1100cm^{-1} " Raman band shifts in an identical fashion with increasing Na^+ content in both the mixed alkali and ion-exchanged glasses. After

Figure 3

- (a) Raman spectra of the $x\text{Li}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ (gl) System (a) $x = 1$;
 (b) $x = 0.5$; (c) $x = 0$.
- (b) Raman spectra of the $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (gl) ion-exchanged in NaNO_3 at
 350°C for various lengths of time: (a) 0 minutes; (b) 1 hr;
 (c) 2 hrs.

Figure 4

- (a) Raman spectra of the $x\text{Li}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (gl) System;
 (a) $x = 0.1$; (b) $x = 0.35$; (c) $x = 0.5$; (d) $x = 1$.
- (b) Raman spectra of the $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (gl) ion-exchanged in NaNO_3
 at 350°C for various lengths of time (unannealed): (a) 24 hrs.;
 (b) 30 minutes; (c) 0 minutes.

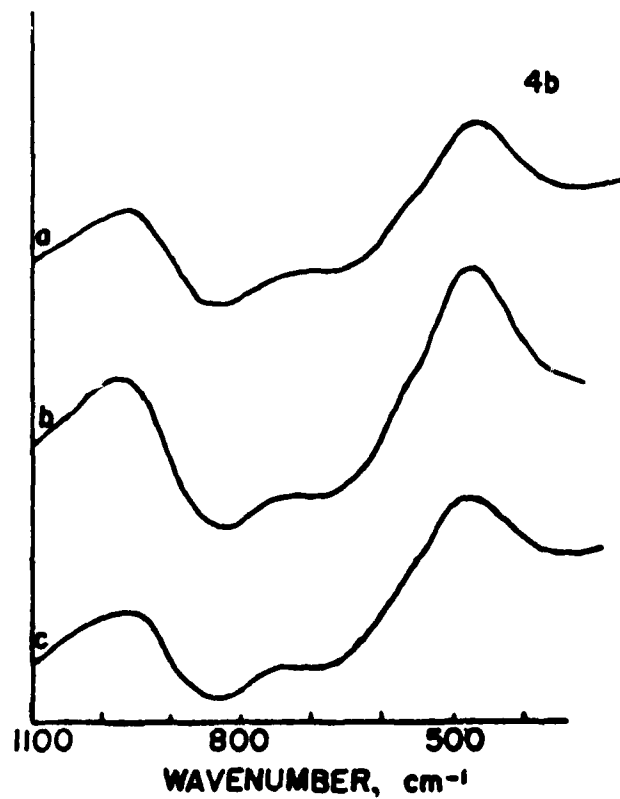
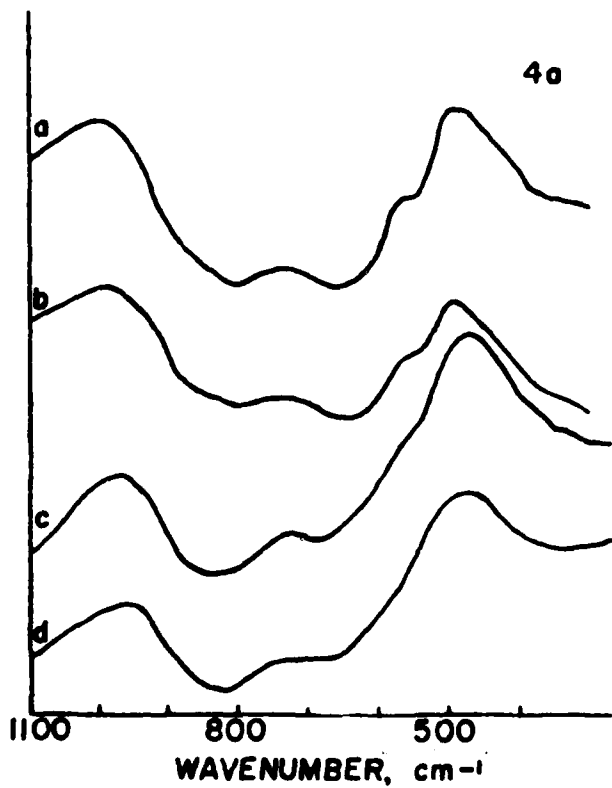
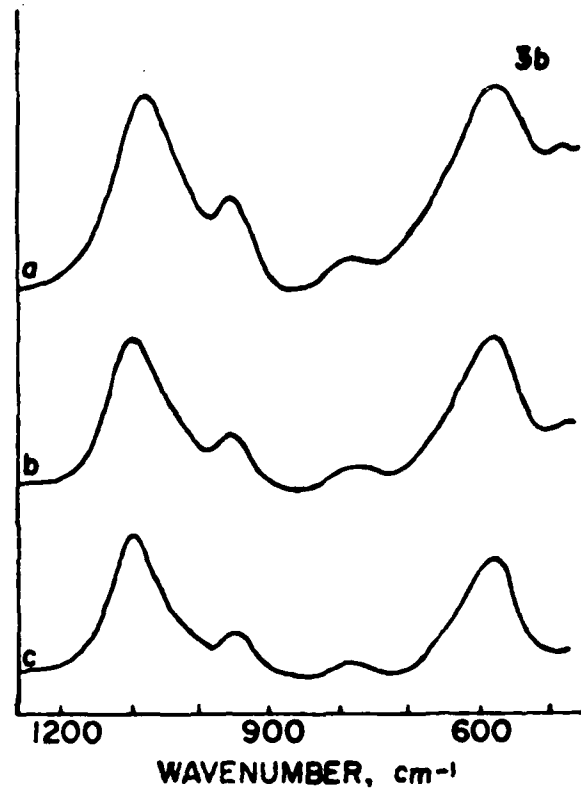
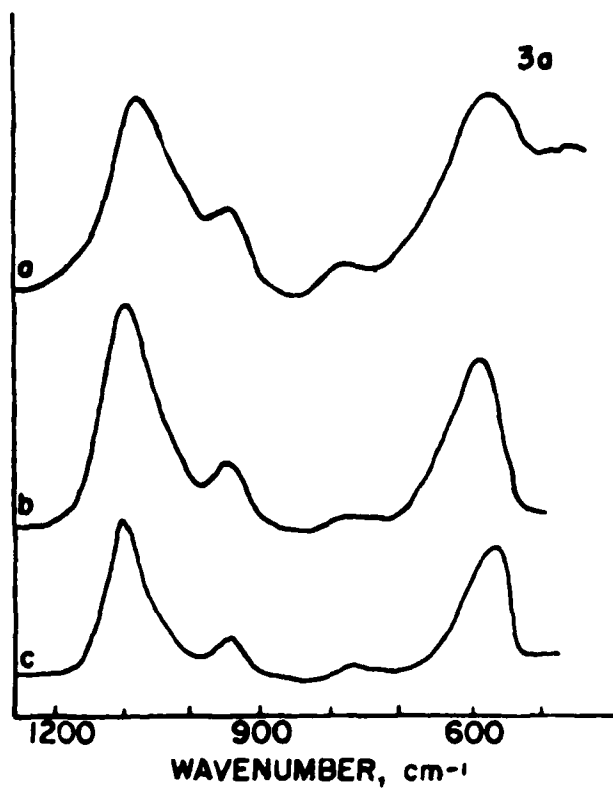


Figure 5

- (a) Frequency of "1100 cm^{-1} " Raman band as a function of x for the system; $x\text{Li}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ (gl).
- (b) Frequency of "1100 cm^{-1} " Raman band for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (gl) as a function of the time of ion-exchange in NaNO_3 at 350°C .

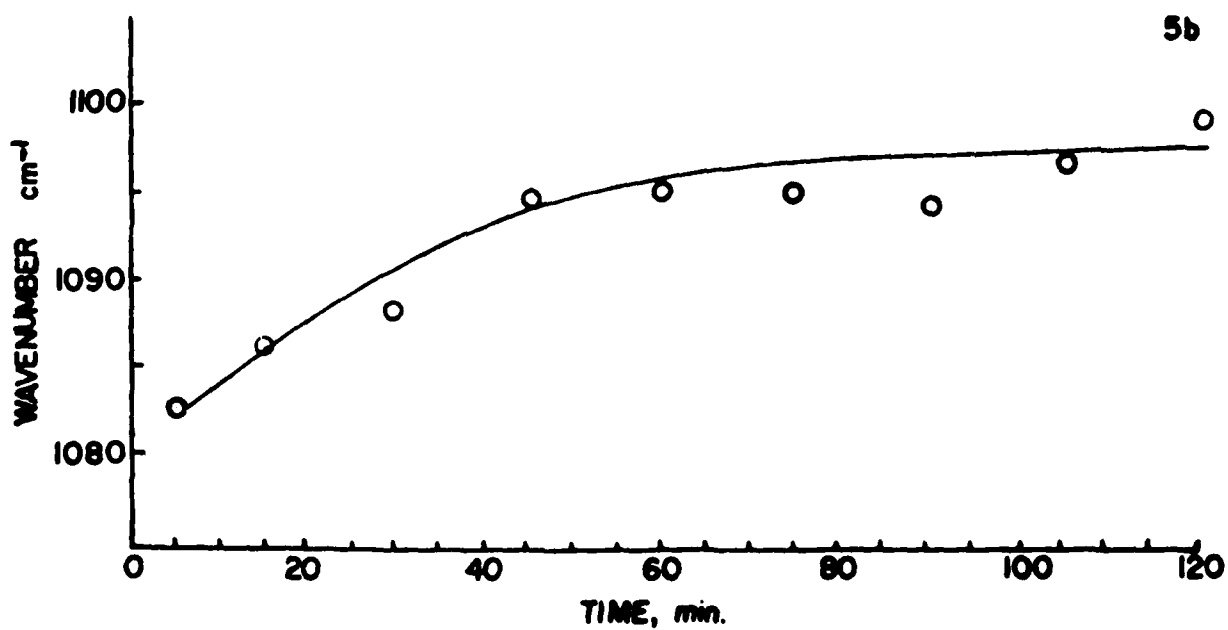
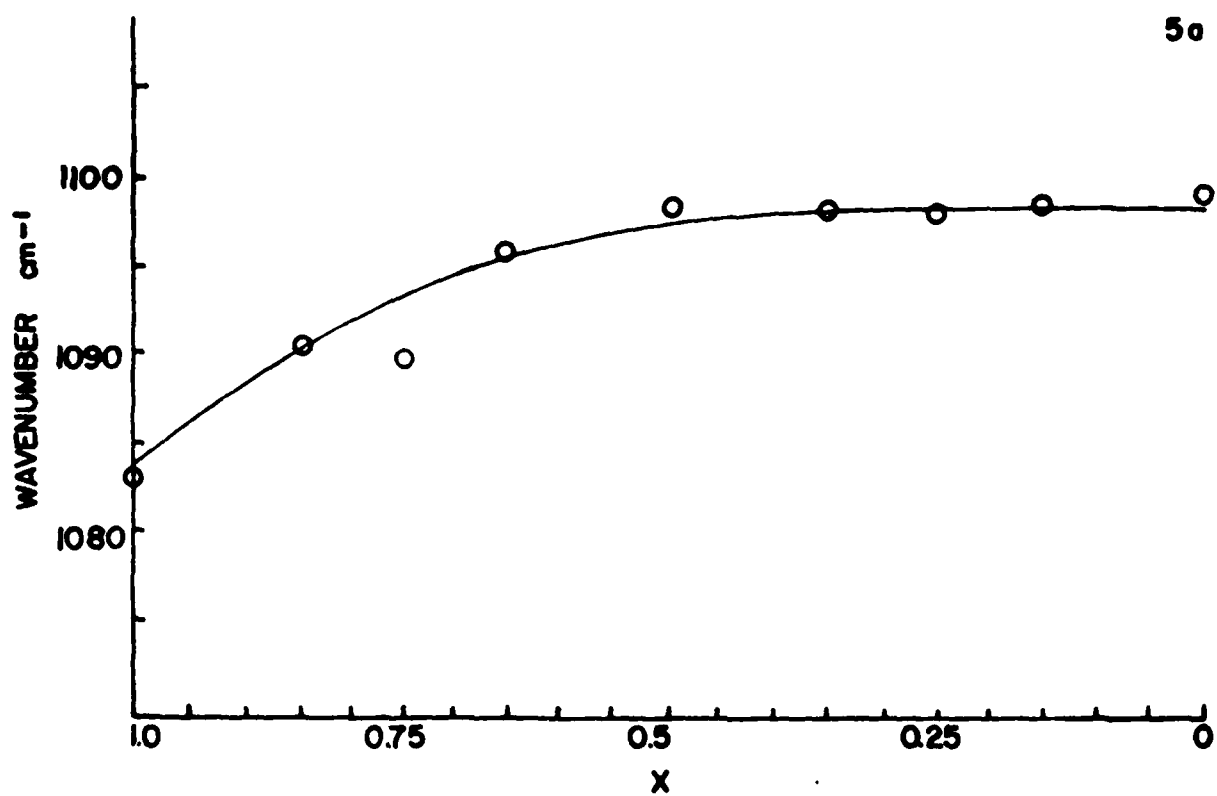
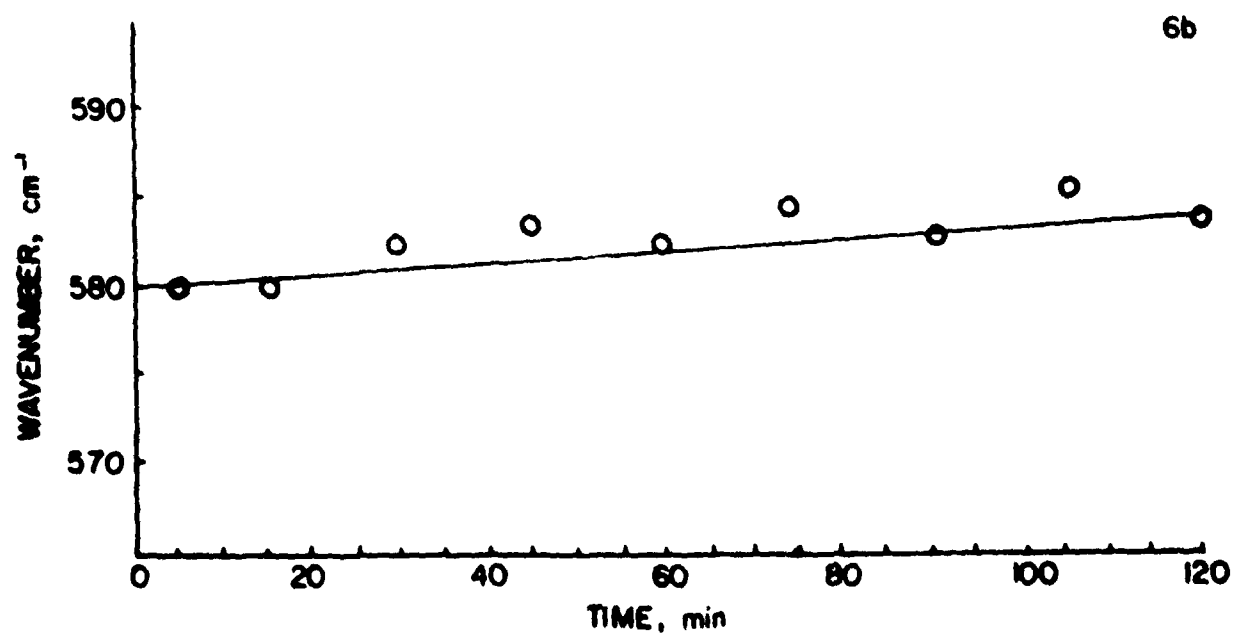
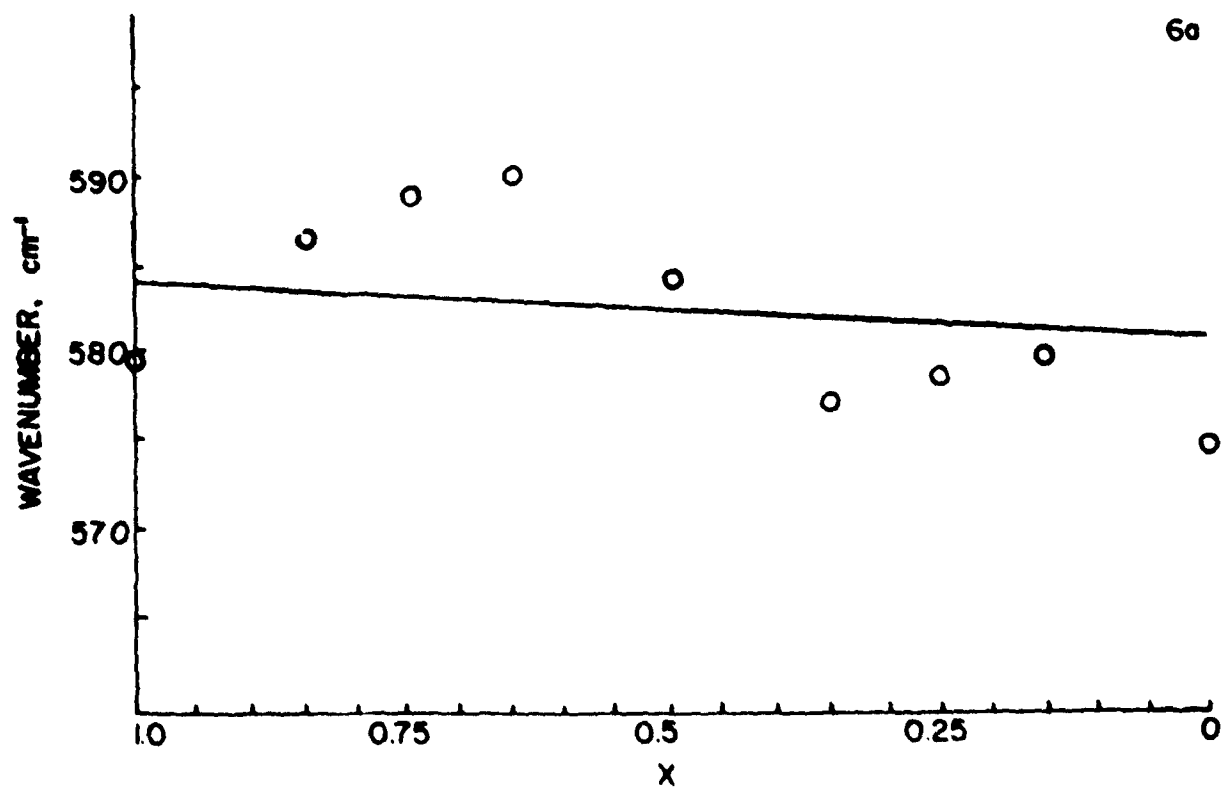


Figure 6

- (a) Frequency of " 575 cm^{-1} " Raman band as a function of x for the system; $x\text{Li}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ (gl)
- (b) Frequency of " 575 cm^{-1} " Raman band for $\text{Li}_2\text{O} \cdot 2\text{SiO}_2$ (gl) as a function of the time of ion-exchange in molten NaNO_3 at 350°C .



one to two hours, it appears that sufficient lithium has been replaced with sodium to cause a shift of this band to nearly the frequency it has in the single alkali glass $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$. While the " 575 cm^{-1} " band does not shift in a pronounced way that is separate from the changes in background scattering, similar changes in background are observed in the 500 cm^{-1} region. It is clear from these spectra that no significant modifications appear to occur to the network structure itself as one cation replaces the other in either the mixed and ion-exchanged alkali disilicate systems. Thus both systems are quite similar. As noted in the Discussion, if the disilicates alone had been studied, the role of network relaxation would not have been apparent, and the effects of ion exchange could be attributed to subtle changes in average cation-network distances and interaction forces.

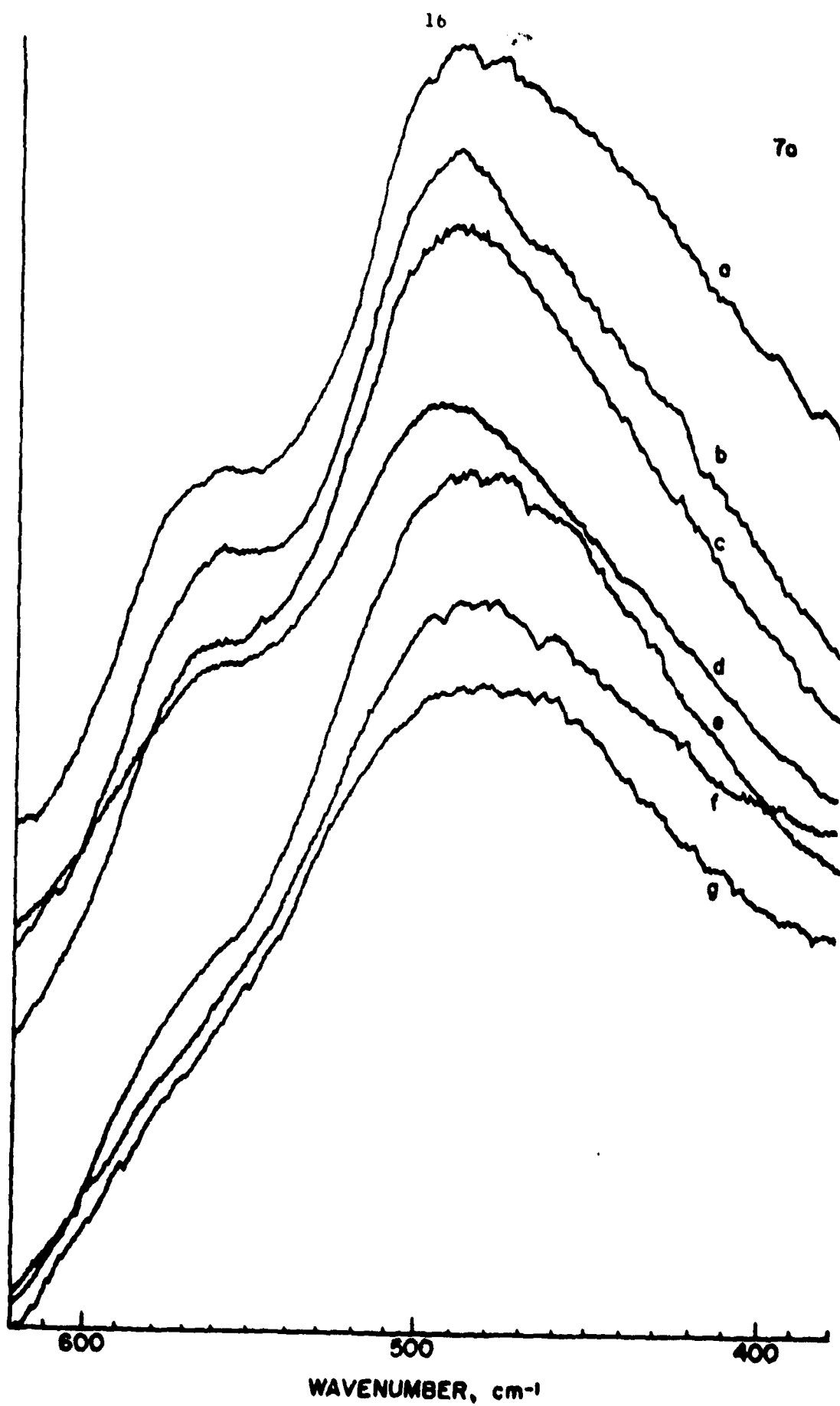
Mixed-alkali Aluminodisilicates. The spectral behavior of the glass system $x\text{Li}_2\text{O} \cdot (1-x)\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, is quite different from that of the disilicates. As is seen in Fig. 4a, three bands stand out in these spectra; and, although these bands do not shift appreciably as x changes, two changes are quite evident.

First, as x decreases, a new band appears at 560 cm^{-1} , as shown in Fig. 4a for $x = 0.1, 0.5$ and 1.0 , and grows as more sodium is substituted for lithium in the glass system. Secondly, as x decreases, the band shape of the lower (492 cm^{-1}) band also changes, with the appearance of a broad lower frequency shoulder. Both of these effects are clearly seen in Fig. 7a. These "new" bands may have been present at low intensity, but concealed under the 500 cm^{-1} band, at high x .

Ion-Exchanged Alkali Aluminodisilicates. As is shown in Fig. 4b, spectral changes observed in the mixed-alkali aluminodisilicate spectra (the growth of the 560 cm^{-1} band and the alteration of shape of the 492 cm^{-1} peak) do not occur for the ion-exchanged glasses of the same composition. For, although there appears to be a hint of a band on the high frequency side of the 500 cm^{-1} peak, it does not change in magnitude with ion exchange for as long a period as

Figure 7

- (a) The $400\text{--}600\text{ cm}^{-1}$ region of the Raman spectrum for the $x\text{Li}_2\text{O}\cdot(1-x)\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ (gl) system; (a) $x = 0.1$; (b) $x = 0.15$; (c) $x = 0.25$; (d) $x = 0.35$; (e) $x = 0.5$; (f) $x = 0.75$; (g) $x = 1$.
- (b) The $400\text{--}600\text{ cm}^{-1}$ region of the Raman Spectrum for the $\text{Li}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ (gl) glasses ion-exchanged for various lengths of time in NaNO_3 at 350°C ; (a) 24 hrs; (b) 30 minutes; (c) 5 minutes; (d) 0 minutes.



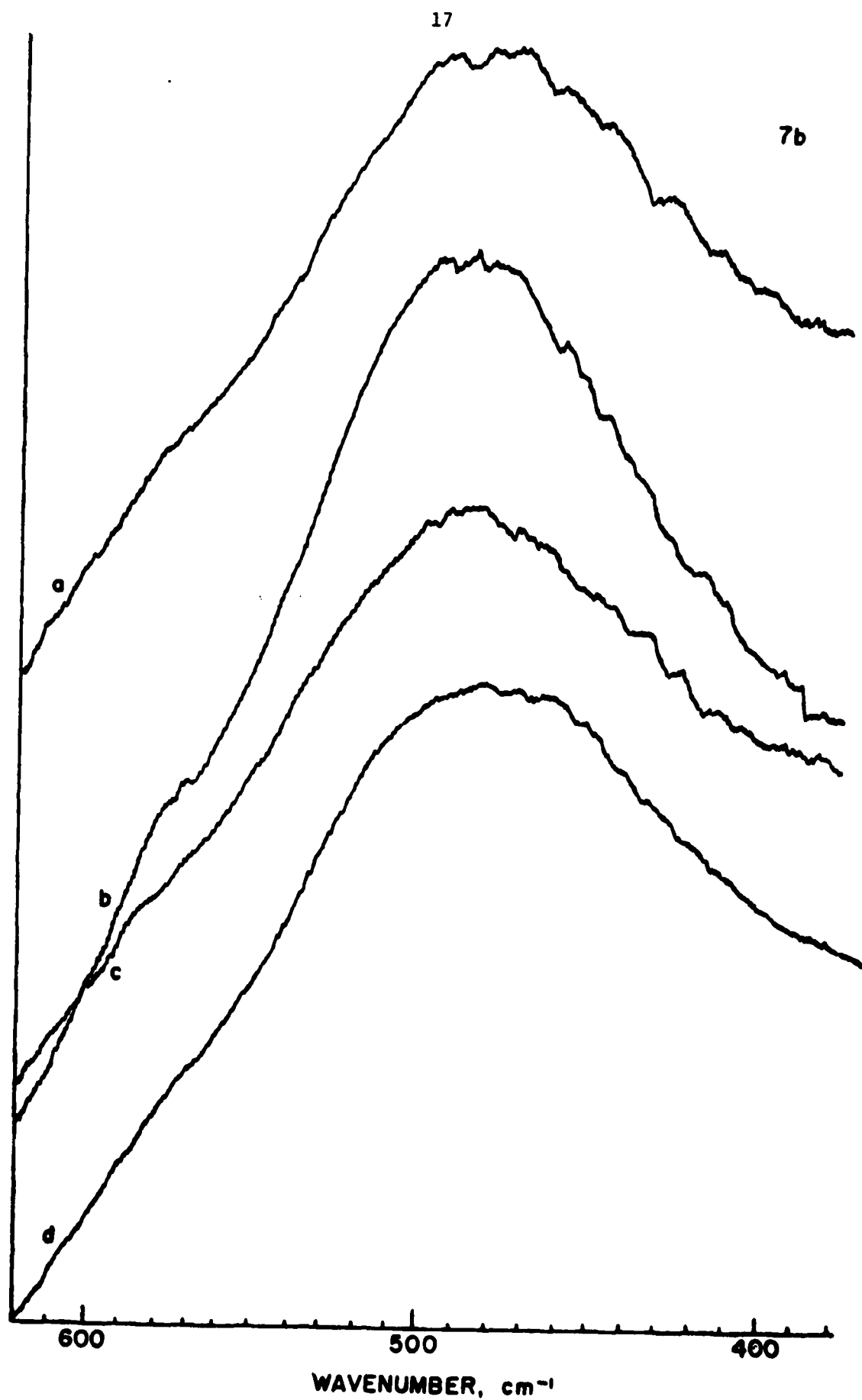
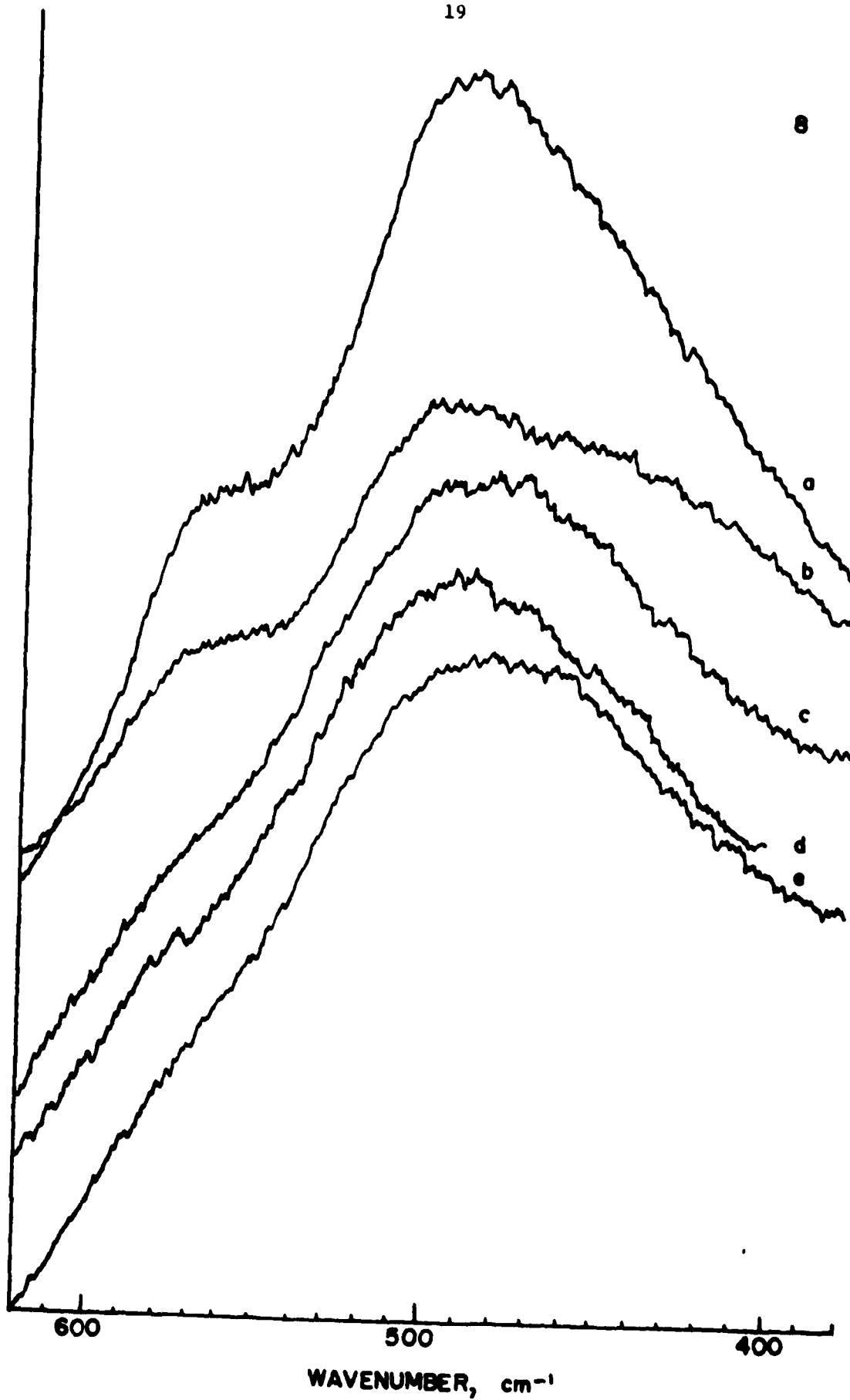


Figure 8

Raman spectra showing the effect of annealing a $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (gl) fiber which had been exchanged in NaNO_3 at 350°C for 24 hours, by comparison with related glasses: (a) conventional mixed alkali glass of the composition $0.25\text{Li}_2\text{O} \cdot 0.75\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, (b) $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ (gl) fiber ion exchanged 24 hr and annealed 24 hr at 590°C ; (c) same as (b) but without annealing, (d) $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_3$ (gl) fiber annealed at 590°C for 24 hr; (e) same as (d) but without annealing.



24 hours.

However, when an ion exchanged fiber is annealed at 590°C for 24 hr., its Raman spectrum develops these characteristics. As can be seen from Fig. 8, an annealed fiber of a glass ion-exchanged for 24 hrs (Fig. 8b) shows the growth of the 560 cm^{-1} band and a shape-change of the broad 492 cm^{-1} maximum. Its similarity to a mixed system can also be seen by comparing Figures 8a and 8b. While they do not have exactly the same shapes, they both show that a structural transformation leading to the appearance of the 560 cm^{-1} band occurs when the network organizes or reorganizes in the presence of both Na^+ and Li^+ .

Spectral Assignments

In order to analyze the effects of the ion-exchange and the mixing processes on the bonding structures of the glasses, it is necessary to assign the Raman spectral features. Although no Raman studies of these or closely related mixed systems have been reported, the spectra of a variety of silicate glasses, including the end-number $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ (8-18), have been published (8,10,11,14). A number of assignments have been suggested for features commonly observed in silicate glasses and they help in identifying certain of the bands shown in Figures 3 and 4, despite the fact that there are clear conflicts between the published assignments.

On the basis of the stoichiometry and crystal structures of $\text{Li}_2\text{O}\cdot 2\text{SiO}_2$ and $\text{Na}_2\text{O}\cdot 2\text{SiO}_2$ (gl), it is known that the silicon atoms are tetrahedrally bound to oxygens and that three of the oxygens per silicon bridge to another silicon. A "chain" structure is found for the crystals. The glassy state is disordered over the long range, but the local structures may be taken to be similar. The disorder of the glass introduces a large number of perturbations on the vibrations, and they contribute to the breadth of the spectral bands, but the general features of the spectrum are attributable to reasonably well separated

vibrational modes. Thus, modes due to terminal Si-O stretching motions, in-chain Si-O-Si stretches, Si-O-Si and O-Si-O bending motions are observed. Although they are coupled, sufficient separation exists in the frequency regime to permit making assignments.

The assignment of the major features of the spectra of $M_2O \cdot 2SiO_2$ (gl) materials is given in Table I. The 1100 cm^{-1} and 945 cm^{-1} bands are due to motions which must be coupled. Although these assignments are consistent with the work of Ferraro (16) and the discussion of Hass (9), they differ from those of Konjnendijk and Stevels (13) in major respects, which include the assignments of the 945 cm^{-1} and 1100 cm^{-1} bands. They suggest that the appearance of a ca 950 cm^{-1} band in a silicate glass is due to a structure containing two non-bridging oxygens on a silicon atom, and that this is consistent with assigning the 1100 cm^{-1} band to the vibration of a structure with one non-bridging oxygen. While that is self consistent, it does not account for the Si-O stretches in the chain and it is inconsistent with our observation that a band analogous to the 1100 cm^{-1} band is observed (1004 cm^{-1}) in alumino silicate glasses having structures with no non-bridging oxygens at all.

The spectral changes observed upon substitution of Na^+ for Li^+ in the $M_2O \cdot 2SiO_2$ glass system are relatively small and are consistent with small changes in the cation-polyanion force field. As shown in our earlier studies (19,20), this results in small changes in both the strengths and angles of the network bands.

The assignments of the Raman bands in the $M_2O \cdot Al_2O_3 \cdot 2SiO_2$ (gl) series are somewhat less straightforward because the spectrum obtained in any given case depends on the preparative conditions. In particular, the 560 cm^{-1} band appears in the spectra of the conventional mixed alkali alumino disilicates

Table I

Assignments of Principal Raman Bands in the 400-1200 cm^{-1} Region for $\text{M}_2\text{O} \cdot 2\text{SiO}_2$
and $\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ Glasses

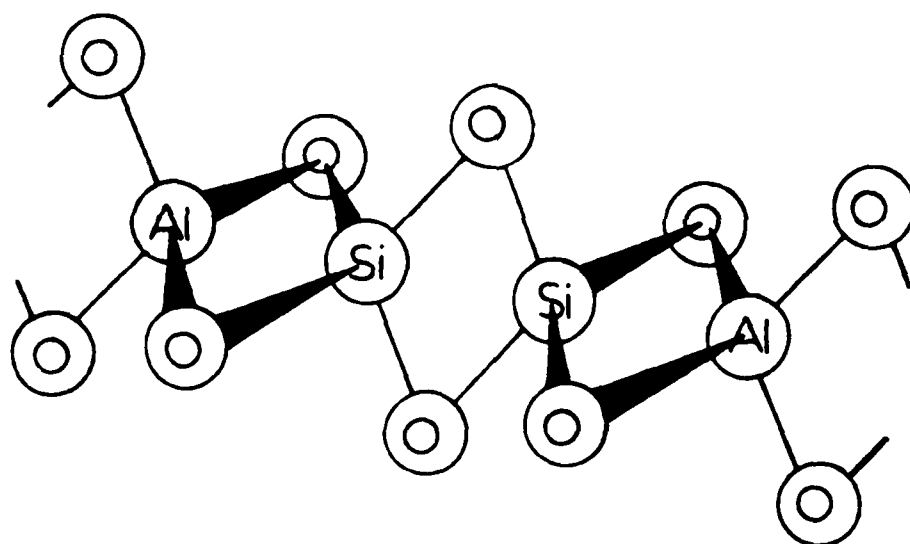
A. $\text{M}_2\text{O} \cdot 2\text{SiO}_2$ Glasses

<u>$\text{Na}_2\text{O} \cdot 2\text{SiO}_2(\text{gl})$</u>	<u>$\text{Li}_2\text{O} \cdot 2\text{SiO}_2(\text{gl})$</u>	<u>Assignment</u>
1100 cm^{-1} (vs)	1083* cm^{-1} (vs)	$\nu(\text{Si-O-Si})$ stretch
945	949	$\nu(\text{Si-O})_t$ stretch
770	780	$\delta(\text{O-Si-O})$ bend
575* (vs)	580 (vs)	$\delta(\text{Si-O-Si})$ bend

B. $\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(\text{gl})$

<u>$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(\text{gl})$ (14)</u>	<u>$0.9 \text{Na}_2\text{O} \cdot 0.1\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$</u>	
1004 cm^{-1} (vs)	1005 cm^{-1} (vs)	$\nu(\text{Si-O-Si}) + \nu(\text{Si-O-Al})$ + $\nu(\text{Al-O-Al})$
736	735	$\delta(\text{O-Si-O}) + \delta(\text{O-Al-O})$
568	560	$\delta(\text{Si-O-Si}) + \delta(\text{Si-O-Al})$ + $\delta(\text{Al-O-Al})$ in new structure (see Fig. 10)
468	492 (vs)	$\delta(\text{Si-O-Si}) + \delta(\text{Al-O-Al})$ + $\delta(\text{Si-O-Al})$ in chain structure.

* This band was reported at 565 cm^{-1} , ref (10).



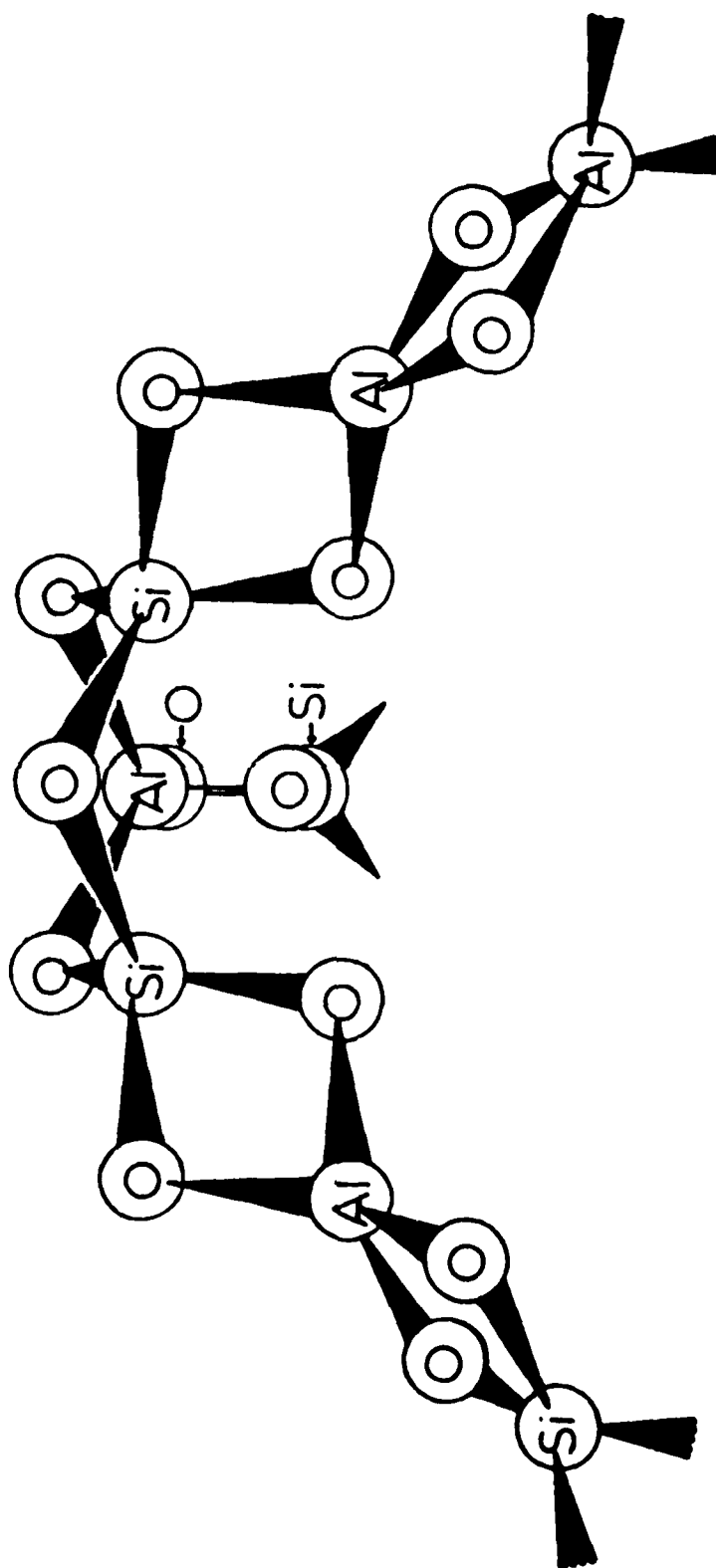
as the Na^+ -content increases and in the spectra of annealed Na^+ -exchanged lithium alumino-disilicate glasses. But, it does not appear in unannealed glasses at any level of exchange. It is associated with a structural feature that is not present in the pure Li^+ -containing glass or any unannealed Na^+ -exchanged glass.

From the stoichiometry of $\text{M}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ it is evident that all oxygens must be involved in bridging, if it is assumed that both Si and Al are tetrahedrally bound and there are no defects. There must be some defects, of course, but it should be noted that introducing six coordinate Al (a commonly proposed kind of defect) does not free oxygens to become terminal rather than bridging. Thus, the principal features of the spectra of the alumino disilicates are attributed to vibrations of structures involving only bridging oxygens.

The ca 1005 cm^{-1} band is clearly due to the symmetric stretch of the A-O-B units (where A and B are Si or Al) and the lower frequency modes are due to bending. The 560 cm^{-1} band which grows into the spectrum is assigned to deformations of a new structural grouping which satisfies the stoichiometry and has similar tetrahedrally coordinated Al and Si atoms with bridging oxygens. This grouping, however, has the characteristic that it is more probable when the larger (Na^+) cation is present and that it is more rigid and thus has a higher deformation frequency. As discussed below, this could be the ring-type chain junction shown in Figure 10. The 560 cm^{-1} band would then be assigned to deformations of the A-O-B angles of this structure.

Discussion

The spectral results on the disilicate and aluminodisilicate glass systems are strikingly different and provide new insight into the relationship between the ionic diffusion and network relaxation (or rearrangement) processes



and the roles they play in glass formation and modification. By analyzing these results it is possible to see that in the aluminodisilicate case the processes can be separated to a considerable extent, but in the disilicates they cannot.

In both the lithium and sodium disilicate glasses, the network structures are apparently about as similar as they are in the crystalline forms of these materials. Thus, whether a given ratio of Na^+ to Li^+ content is achieved by ion exchange or by conventional melt mixing to form mixed alkali glasses, nearly the same network results. The major change accompanying the ion exchange process in this case is simply diffusion of the ions. Naturally small changes in average cation-network separation, cation-cation interactions, and other interactions must also accompany the process, but the Raman spectra indicate that they do not cause significant network modifications. Therefore, the ion exchanged glasses in which the ions have distributed themselves randomly can be thought of as having mechanical properties that are similar to those of the mixed alkali glasses for the simplest of reasons; they are very similar glasses.

In the case of ion exchanged disilicate glasses in which the ions do not have sufficient time to distribute themselves as randomly as possible, it is clear that a cation concentration gradient exists and decreases in exchange-ion concentration from the surface into the bulk. They may have mechanical behavior ranging from that of a perturbed pure single alkali glass to that of a composite material. Since the network spectral features are not very different for the Na^+ and Li^+ forms of the disilicates, such gradients do not show up in the spectra even though the spectral sampling method exposes the entire sample cross section. The far infrared spectrum of ground, ion-exchanged glasses

show that the cation motion vibrations are similar to those in the single alkali glasses.

The fact that the ion-exchanged and conventionally mixed alkali disilicates are spectroscopically similar does make it possible to assert that their mechanical properties should be similar, and, specifically, that a "mixed alkali peak" or HTP should appear in the ($\tan \delta$ vs x) mechanical loss spectrum. However, it does not directly provide an understanding of the origin of this feature, and it does not address the question of whether network relaxation is necessary to make the two forms of glass of the same overall composition closely similar.

On the other hand, the study of the aluminodisilicate glasses provides more insight into the nature of the processes involved.

The process of making a mixed alkali glass by ion exchange that is equivalent to one that is made by conventional melting can be divided conceptually into the cation exchange (diffusion) process and the network relaxation process. The first can lead to a spatial distribution of cations throughout the bulk that is about the same in glasses prepared either way. The second can lead to a network structure in an exchanged glass that is equivalent to the one achieved in the mixed alkali melt. Although these processes are never completely separable, a significant separation of them was achieved in these experiments.

As discussed above, the spectra of $\text{Li}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2(\text{gl})$ fibers that are about 75% exchanged with Na^+ do not show the 560 cm^{-1} Raman band that appears in the spectra of mixed alkali aluminodisilicate glasses of the same composition. Since exchange at this level assures extensive (though non-uniform) distribution of Na^+ ions throughout the sample, it is clear that the 560 cm^{-1} band would appear in the spectrum if it were due simply to the presence of Na^+ at sites

in the unaltered network. Thus, mixing the alkali ions does not cause the glass to achieve a state equivalent to that of the conventionally melted mixed alkali glass.

However, it does cause the appearance of a mechanical loss peak (HTP) similar to the one observed for the mixed alkali glass (Fig. 2b). This clearly means that the presence of a distribution of dissimilar cations is associated with the HTP peak regardless of whether the network has reached the state it has after either melting or annealing. It does not mean that the motion of this collection of dissimilar cations is, in fact, the process that causes the mechanical loss, but only that their presence is an essential feature. Nor does it mean that their presence explains the (HTP) mechanical loss, because such a loss peak for an ion exchanged glass does not always vary with composition (i.e. T_p vs x) in the way it does for a conventional mixed alkali glass.

Thus, we may conclude so far from these data that the presence of a distribution of dissimilar cations, however attained, satisfies a necessary condition for a (HTP) mechanical loss peak but does not fully explain it. Were it to be both a necessary and sufficient condition it would also explain its variation with x .

When an ion-exchanged (at 75% Na^+ , for example) aluminodisilicate glass is annealed at 590°C for 24 hr, the 560 cm^{-1} band appears. The network rearrangement accomplished by this annealing results in formation of the structures favored by the presence of Na^+ . The similarity of the Raman spectrum of the ion exchanged glasses (8b) to that of the melted mixed alkali glass (8a) indicates that the Na^+ ions assist in the rearrangement which yields such structures. As depicted in Fig. 10, the formation of chain junctions leads to ring structures that are more open and provide an energetically and sterically more favorable position for the Na^+ than does the tighter chain structure

apparently favored by the smaller Li^+ ion. A reasonable low energy path to achieve this structure can be constructed in which the Na^+ assists in the postulated bond rearrangements.

In previous work the 560 cm^{-1} band in aluminosilicates was attributed to defects in the glass networks (15), producing Si and Al atoms attached to one or more non-bridging oxygens. Acknowledging the presence of a small number of such defects, since the stoichiometry requires that all oxygens in the network be bridging, the proposed new structural feature seems most reasonable. The effect such a ring formation would have on the spectrum would have to be calculated to be evaluated with certainty, but it is quite likely that it would include the appearance of two new bending modes in the 500 cm^{-1} region. The more constrained angles of the ring (B) are expected to make one such deformation appear at a frequency higher than the 490 cm^{-1} band, and we have assigned the 560 cm^{-1} band to that mode. The α angles may be more easily deformable and give rise to the increased scattering intensity below 490 cm^{-1} .

From these experiments on the aluminodisilicates, then, we conclude that the ion exchange leads to a distribution of dissimilar cations and an accompanying rise of a mechanical loss peak (HTP) which is similar to that of a mixed alkali glass, but that it arises without a network structural change. At higher temperatures, achieved by annealing or melting, a network structural change occurs separately. This rearrangement or relaxation resulting from annealing is a change toward the structure formed in and quenched from the melt of the same composition. The rates of the ionic diffusion and network change are sufficiently different and their spectral effects are different enough that the kinetics of the two processes can be studied separately.

Although the presence of dissimilar cations is essential to the appearance

of the HTP, the HTP involves network rearrangements. Moreover, the segment of the network whose relaxation gives rise to the HTP must vary with composition for T_p of the HTP to vary. Thus, we can postulate that a network rearrangement becomes probable and gives rise to a mechanical loss peak when a large number of equivalent configurations is available to the system; i.e., when its configurational entropy increases. However, the temperature dependence of the peak is a function of both the nature of the network and the size of the rearranging segment required to sample enough points in the configuration space for the rearrangement to become probable.

Acknowledgment

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