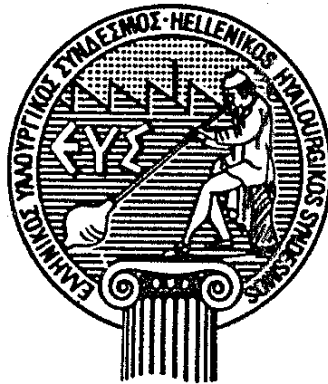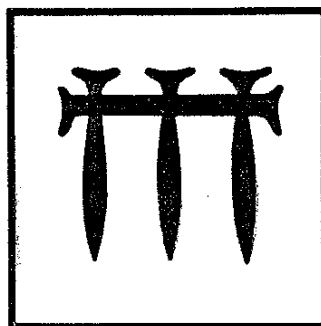# INTERNATIONAL SYMPOSIUM
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ALKALI SITES IN SILICATE GLASSES

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The nature of sites occupied by metal ions in glass can be investigated by infrared spectroscopy. This work presents the results of an infrared reflectance study of alkali silicate glasses of the type $xNa_2O.(1-x)SiO_2$ ($0.1 \leq x \leq 0.45$) and $M_2O.2SiO_2$ (M=alkali). The analysis of the far infrared absorption profiles showed the existence of two bands with frequencies scaling approximately with the inverse square root of cation mass. It was therefore concluded that silicate glasses, similarly to borates, are characterized by two distinct site distributions for the alkali cations. The frequencies of the two cation motion bands were found to increase with sodium oxide content. This was attributed to the increasing charge density of the cation-hosting sites, as a result of the formation of highly charged silicate species.

INTRODUCTION

Addition of a modifier oxide to a glass former causes progressive changes of the glass structure. It has been suggested that the need of the modifier cations to create their own suitable coordination is one of the driving forces that determine the nature of structures assumed by the glass network (1). The establishment of characteristic environments/sites of the metal ions in glass has been revealed by various techniques, including far infrared measurements (2,3), EXAFS studies (4) and neutron scattering experiments (5). The elucidation of the nature of sites occupied by metal ions in glass is an important factor for understanding properties such as the ionic conductivity (6-8), the glass basicity (9) and the operation of color centers or lasers (10,11).

Recent infrared studies of alkali borate glasses have shown that alkali cations are present in two major distributions of anionic site environments (12,13). These two types of sites differ mainly in their electron density, i.e. they exhibit different local basicities (9,14). It is of interest to note also that mobile cations were found to occupy mainly the higher basicity sites (9).

While far infrared spectra of alkali silicate glasses have been reported by a number of authors (15-21), no systematic investigation of the cation-site interactions in such systems has been undertaken so far. This work reports on the findings of an infrared reflectance investigation of alkali silicate glasses of the type $xNa_2O.(1-x)SiO_2$ ($0.1 \leq x \leq 0.45$) and $M_2O.2SiO_2$ (M=alkali). The main purpose of this work is to investigate the alkali sites in silicate glasses and, therefore, to explore the possibility that our previous findings regarding borate glasses have some generality beyond these glass systems. In this context, we have studied the effect of alkali content and type on the alkali-site interactions, as well as the structure of the glass network which provides the sites for alkali ions.

EXPERIMENTAL

The glasses investigated were prepared from stoichiometric mixtures of alkali carbonates and SiO_2. Melting was performed in platinum crucibles in the temperature range 1000-1400 °C depending on composition. After approximately two hours, the melt was cast into preheated at 300 °C steel molds to form discs of 2 cm in diameter and 3 mm in thickness. All samples prepared were clear and transparent. Those used for infrared
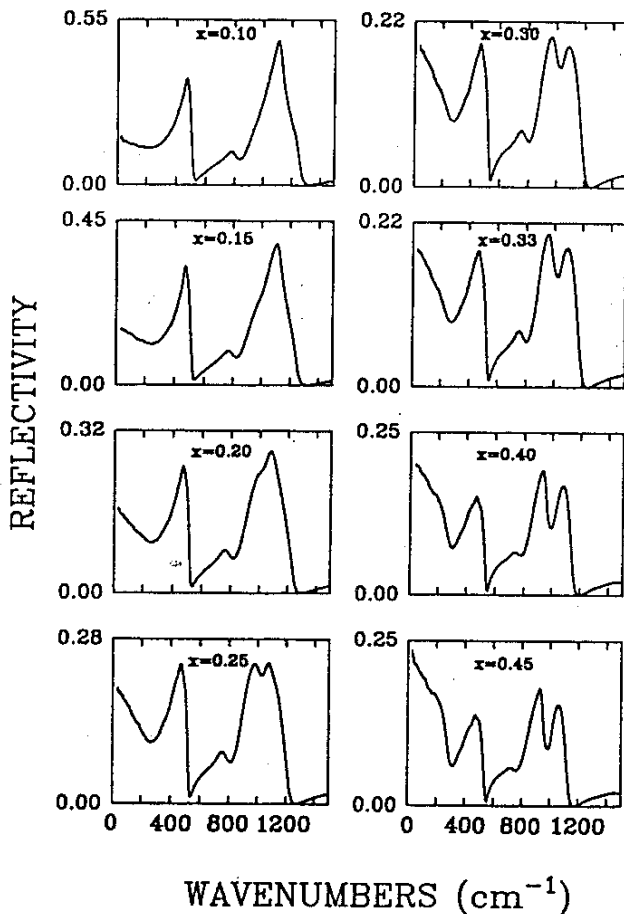
Fig.1 Infrared reflectance spectra of sodium-silicate glasses $xNa_2O.(1-x)SiO_2$
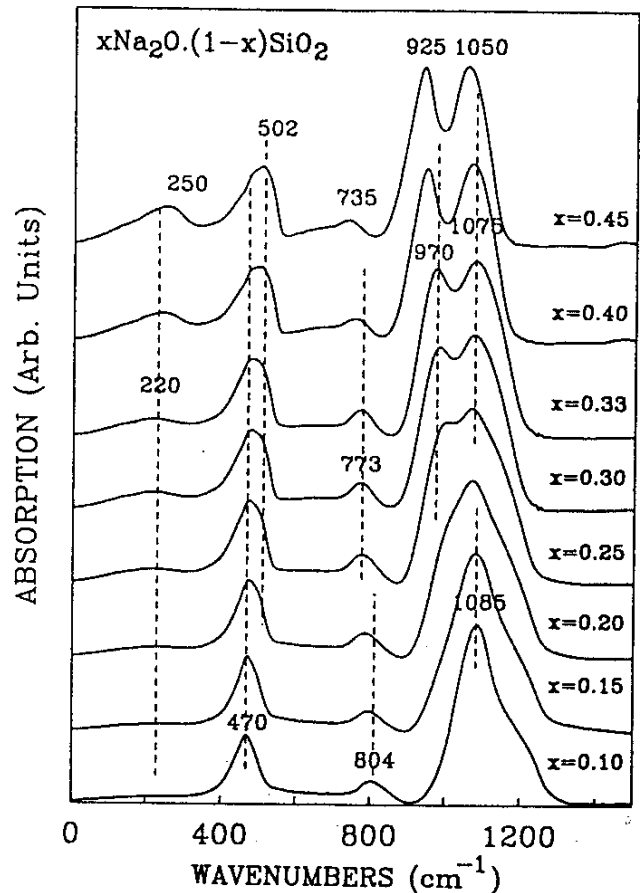
Fig.2 Absorption coefficient spectra of sodium-silicate glasses $xNa_2O.(1-x)SiO_2$

measurements were ground flat and polished on one side. To minimize surface hydrolysis, the samples were kept in desicators and repolished a number of times prior to spectral acquisition and until reproducible reflectivity data were obtained.

Infrared spectra were measured on a Fourier-transform vacuum spectrometer (Bruker 113v). An 11° off-normal specular reflectance attachment, with a high reflectivity aluminum mirror as reference, were utilized for reflectivity measurements. A combination of sources, detectors and beam splitters was employed to achieve continuous spectral coverage in the range 30-4000 cm^{-1}. Each spectrum is the average of 200 scans at 2 cm^{-1} resolution. The reflectance spectra were transformed by the Kramers-Kronig method to obtain the optical and dielectric properties required for the calculation of absorption coefficient spectra (14).

RESULTS

The infrared reflectance spectra of sodium-silicate glasses are shown in Figure 1 for sodium contents spanning the range $0.1 \leq x \leq 0.45$. For the x=0.1 glass composition a spectrum quite similar to that of vitreous SiO_2 (22) has been obtained, except for its small reduction in reflectivity. Increase of the Na_2O content causes further reduction in reflectivity and drastic changes of the spectral profiles. In particular, the peak at 1100 cm^{-1} develops a shoulder at ca 980 cm^{-1} (x≤0.2) and this becomes eventually the main reflectivity peak (950 cm^{-1}) for high values of x. A similar behavior was observed in earlier mid infrared absorption (23,24) and reflectance (25, 26) studies of sodium- silicate glasses.

Increasing x causes also the progressive increase of the far infrared reflectivity, which dominates the spectrum of glasses with high sodium content. While there are no well defined maxima in the far infrared reflectivity spectra, the absorption coefficient spectra (Figure 2) illustrate clearly the development of a far infrared feature at ca 220 cm^{-1}. The intensity and frequency of this band increase with Na_2O content. Similar far infrared

features are exhibited by the spectra of all alkali silicate glasses, as shown in Figure 3 for the disilicate composition (x=0.33 and M=Li, Na, K, Cs). The frequency and bandwidth of the far infrared peak increase upon decreasing the alkali size, while for M=Li this feature is not resolved due to its considerable overlapping with the band at *ca* 500 cm^{-1}.

DISCUSSION

The Structure of the Silicate Network

Information about the structure of the silicate network and its dependence on the sodium content can be obtained from the mid infrared spectra (400-1400 cm^{-1}). Three spectral regions (400-550 cm^{-1}, 700-850 cm^{-1} and 850-1300 cm^{-1}) can be seen in the spectra depicted in Figure 2. The low frequency envelope (400-550 cm^{-1}) can be attributed to the rocking motion of Si-O-Si bridges, while the bending mode of the same bridges is responsible for absorption in the 700-850 cm^{-1} region (27). The high frequency envelope (850-1300 cm^{-1}) originates from the asymmetric stretching vibrations of Si-O-Si bridges (27) and Si-O$^-$ dangling bonds of Q^n silicate tetrahedra (n is the number of bridging oxygens per silicon tetrahedron) (23, 28).

Based on the results of previous Raman (29-31) and infrared (23,28) studies of modified silicate glasses, we assign the bands at *ca* 1085, 1075 and 935 cm^{-1} to Q^4, Q^3 and Q^2 sites, respectively. Therefore, the evolution of the high frequency envelope with sodium oxide content (Figure 2) shows a progressive depolymerization of the silicate network by increasing the number of non-bridging oxygens per silicon site.

The behavior of the 400-550 cm^{-1} envelope is also consistent with this structural evolution. The frequency of the rocking motion of Si-O-Si linkages increases upon increasing network depolymerisation. This is in accord with the composition dependence of the Raman active vibration of Si-O-Si bridges (a mixed stretching-bending mode) which appears in the same frequency range (29).

The mid infrared and Raman results regarding the structure of the glass network in sodium-silicate glasses are fully compatible with the findings of ^{29}Si NMR (32,33) and XPS (34) studies on similar glass compositions.
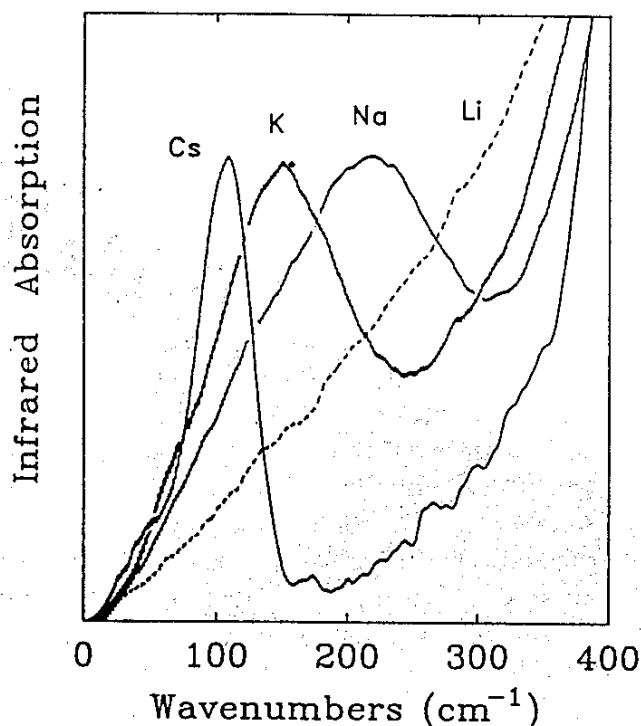

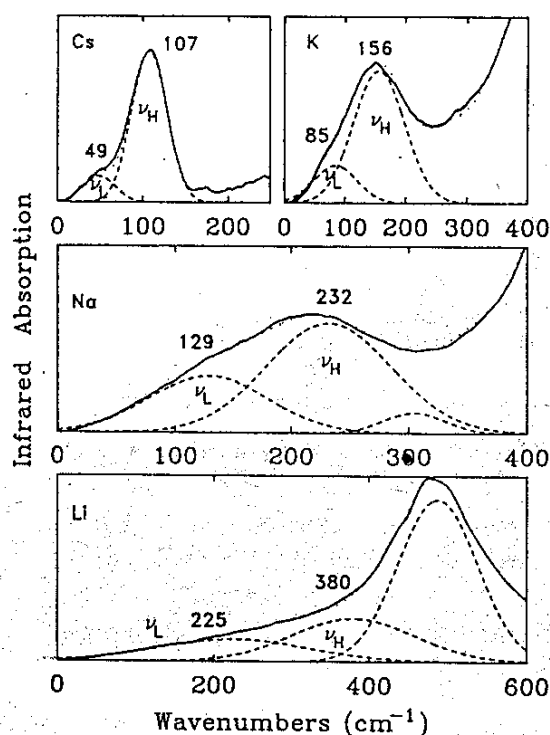Fig.3. Far infrared spectra of alkali-disilicate glasses 0.33M$_2$O.0.67SiO$_2$.

Fig.4. Deconvolution of the far infrared spectra of 0.33M$_2$O.0.67SiO$_2$ glasses. The simulated spectra are shown by dotted lines.

The Localized Vibrations of Alkali Metal Ions

Intense bands in the far infrared spectra of ionic glasses have been assigned to vibrations of metal ions in their localized sites in the glass (15). As shown in Figures 2 and 3, the far infrared profiles of the alkali silicate glasses are asymmetric, thus suggesting the existence of more than one band. To investigate the origin of such asymmetries we have deconvoluted the far infrared profiles, using techniques applied previously to borate glasses (12-14) and employing the minimum number of bands to achieve a reasonable fit of the experimental spectra. For the case of Li, Na and K glasses it was necessary to consider also the silicate band at ca 500 cm^{-1} because of its overlapping with the alkali motion band.

The results of the deconvolution are shown in Figure 4. It is clear that the far infrared asymmetry can be well accounted for by the presence of two Gaussian type components with frequencies designated by v_H and v_L. The weak band resolved at 305 cm^{-1} for the Na glass could originate from a silicate deformation mode (see below). Figure 5 shows that the far infrared frequencies v_H and v_L scale with the inverse square root of the mass of the alkali ion. It is therefore reasonable to attribute both bands to vibrations of alkali ions in their network sites. This result is similar to that obtained for alkali borate glasses (12-14) and suggests that the observed asymmetries of the far infrared profiles present a universal structural characteristic of glasses modified by ionic oxides.

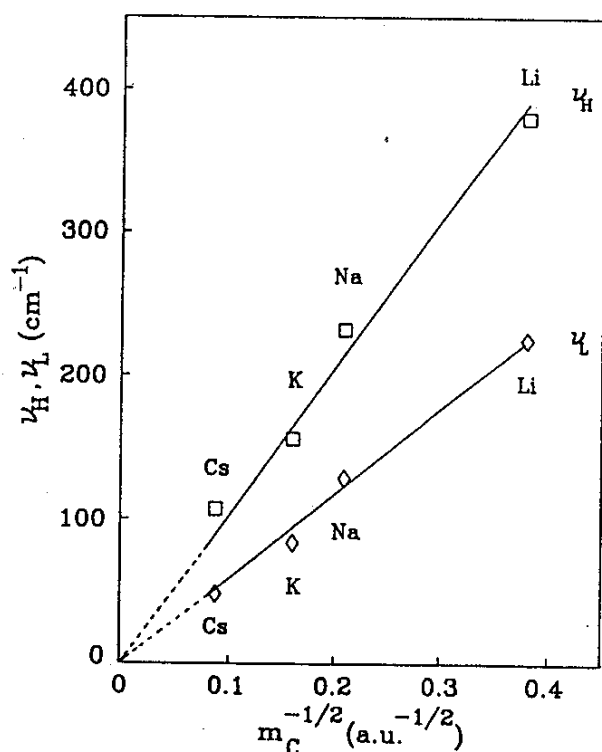The origin of such a universal characteristic cannot be traced to the details of the network structure, since the latter depends strongly on the nature of the glass forming oxide, as well as on the modifier oxide content. It was argued elsewhere that the two far infrared component bands indicate the presence of two different distributions of anionic site environments, which may signal the presence of structural inhomogeneities (12-14). It is of interest to note that computer simulation studies have given evidence for the existence of inhomogeneities in alkali silicate glasses (35-37), which are manifested by an inhomogeneous distribution of alkali ions in alkali-rich and silica-rich pseudophases. Because of differences in site charge density, alkali ion motions in the former pseudophase would occur at higher frequencies (v_H) than those in the silica-rich pseudophase (v_L).

The effect of sodium content on the ion motion bands is shown in Figure 6 where deconvoluted far infrared spectra of representative compositions are presented. Besides the two Na motion bands with frequencies v_H and v_L, a third component is resolved for $x<0.40$ with relative intensity decreasing upon increasing sodium content (see also Fig.4, M=Na).

Fig.5. Cation-motion frequencies versus $m_C^{-1/2}$ in $0.33M_2O.0.67SiO_2$ glasses, where m_C is the cation mass. High- (v_H) and low-frequency (v_L) band maxima were obtained by deconvoluting the far infrared spectra (see Figure 4).

This ca 305 cm^{-1} feature was not resolved in the x=0.45 glass spectrum of Figure 6 because it is probably overmasked by the enhanced 254 cm^{-1} component. We attribute the ca 305 cm^{-1} band to a silicate network deformation mode (38).

Despite the large variation of the silicate network structure with Na_2O content (Figure 2) the far infrared envelope could be always simulated by two Na ion motion bands.

These findings strengthen the argument that the presence of two major distributions of ionic site environments is beyond the details of the glass network structure. Of course, the change of the latter with Na_2O content affects the sites hosting Na ions. This is demonstrated in Figures 6 and 7 where the increase of the Na motion frequencies upon increasing x is evident. This result is in agreement with earlier studies on borate (12) and silicate (19) glasses and can be attributed to the progressive increase of the corresponding site charge density resulting from the depolymerization of the silicate network.
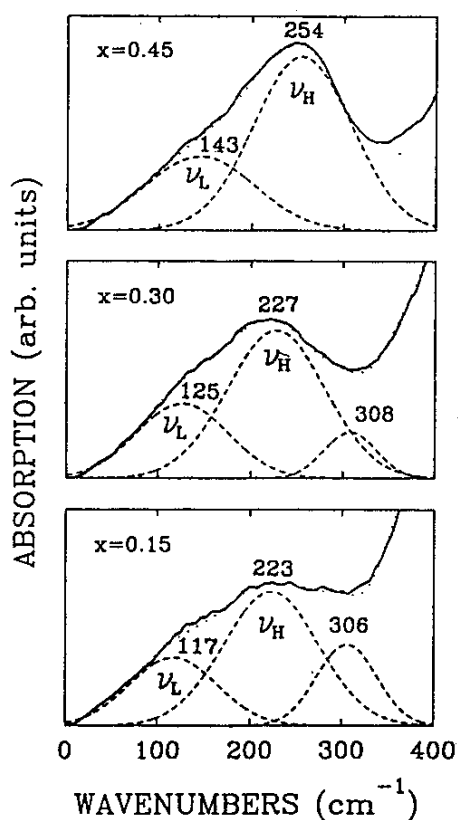

Fig.6. Deconvolution of the far infrared spectra of $xNa_2O.(1-x)SiO_2$ glasses. The simulated spectra are shown by dotted lines.

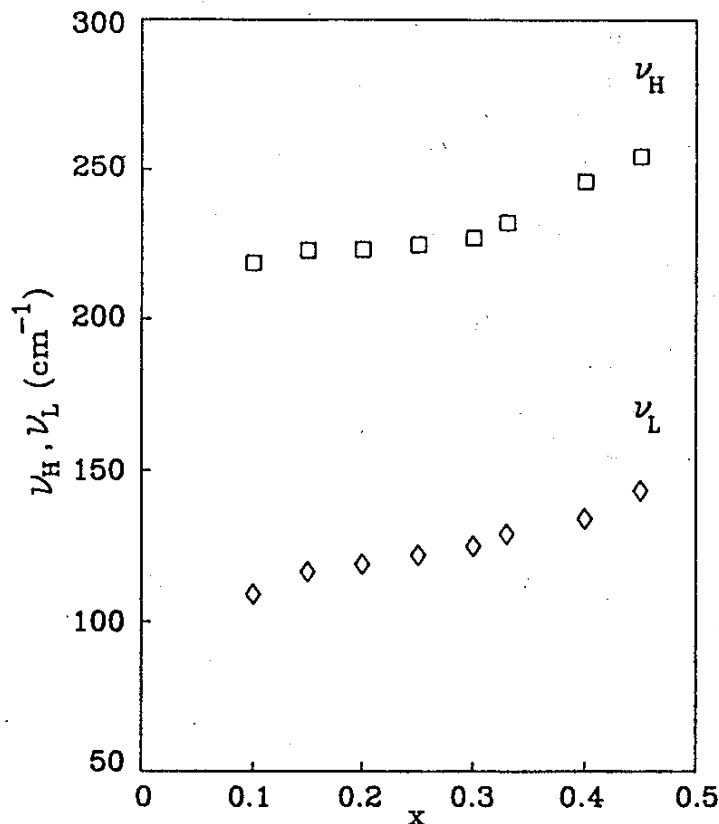*Fig.7. Composition dependence of the sodium ion motion fraquencies in $xNa_2O.(1-x)SiO_2$ glasses.*

The presence of sites with different charge density would subsequently imply differences in their local optical basicity (9). This aspect of the work is in progress and will be reported elsewhere.

CONCLUSIONS

It has been shown that the far infrared spectra of alkali silicate glasses can be simulated by two bands assigned to vibrations of alkali ions in two distributions of anionic environments. The nature of the environments surrounding the metal ions was found to depend on the alkali content. In particular, the anionic charge of the ion-hosting sites increases with alkali content as a result of network depolymerization. The asymmetries of the far infrared profiles which give rise to the two ion motion bands appear to present a universal behavior of modified oxide glasses. The origin of this can be traced to structural inhomogeneities inherent to such glasses.

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