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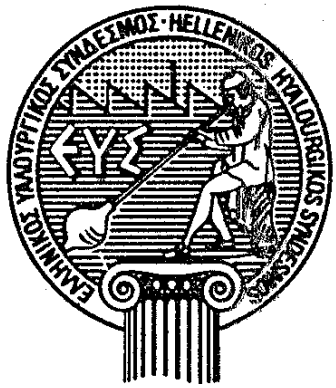

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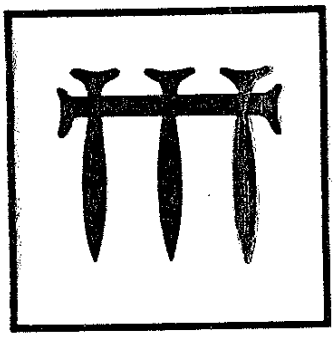

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STRUCTURAL ASPECTS OF THE MIXED ALKALI EFFECT

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Structural aspects of the mixed alkali effect have been investigated in borate glasses by employing infrared reflectance spectroscopy. The nature of sites occupied by alkali metal ions was studied and found to vary systematically with alkali mixing and to lead to new ion-site bonding requirements. These are fulfilled by local structural rearrangements, like the isomerization of boron-oxygen tetrahedra into borate triangles with non-bridging oxygens. Such effects appeared enhanced with increasing the difference between the dissimilar alkalis, or the total alkali content.

1. INTRODUCTION

In the well known mixed alkali effect the presence of a dissimilar alkali metal ion causes a large non-linear decrease in ionic conductivity. Despite the universality of this effect and the large number of theories proposed for its explanation its origin remains highly controversial (1). A number of earlier theories have proposed the presence of dissimilar alkalis in neighbouring sites, i.e. the formation of network-mediated "pairs" of unlike alkalis (2-6). It was further argued that "pairs" of dissimilar alkalis are energetically favoured compared to "pairs" of similar alkalis, with this leading directly to the decrease of ion mobility. Recent theoretical advances on the mixed alkali effect by Bunde, Maass and Ingram have focussed also on the presence of sites suitable for each mobile ion (7,8). Such ion sites were assumed to retain their identity in the mixed alkali glass, and this was shown to lead to mismatch and memory effects and therefore to influence the ion transport process.

As it appears from the above, the detailed knowledge of the kind of sites occupied by metal ions in mixed alkali glasses is an important factor for a better understanding of the mixed alkali effect. Previous studies from this laboratory have demonstrated that infrared spectroscopy can be successfully employed to investigate ion-site interactions in various glass systems (9-14). In this report we present results of an infrared reflectance investigation of mixed alkali glasses (MAG's) in the system: $xM_2O.(1-x)M'_2O.nB_2O_3$ (M, M' = alkali and n = 5, 2, 1.2). Fourier-transform infrared reflectance spectra have been recorded over a broad frequency range and analysed in order to investigate the dependence of the glass structure and the ion-site interactions on the alkali substitution ratio (x), the difference between dissimilar alkalis (M, M') and the total alkali content.

2. EXPERIMENTAL

Glasses were prepared from the stoichiometric amounts of anhydrous B_2O_3 and metal carbonates by conventional melting techniques. Infrared spectra were recorded in the reflectance mode on a Bruker 113v spectrometer. Details of sample preparation and data acquisition and analysis can be found elsewhere (10).

3. RESULTS AND DISCUSSION

3.1 The Structure of the Glass Network.

Typical infrared absorption coefficient spectra are shown in Fig. 1 for MAG's in the

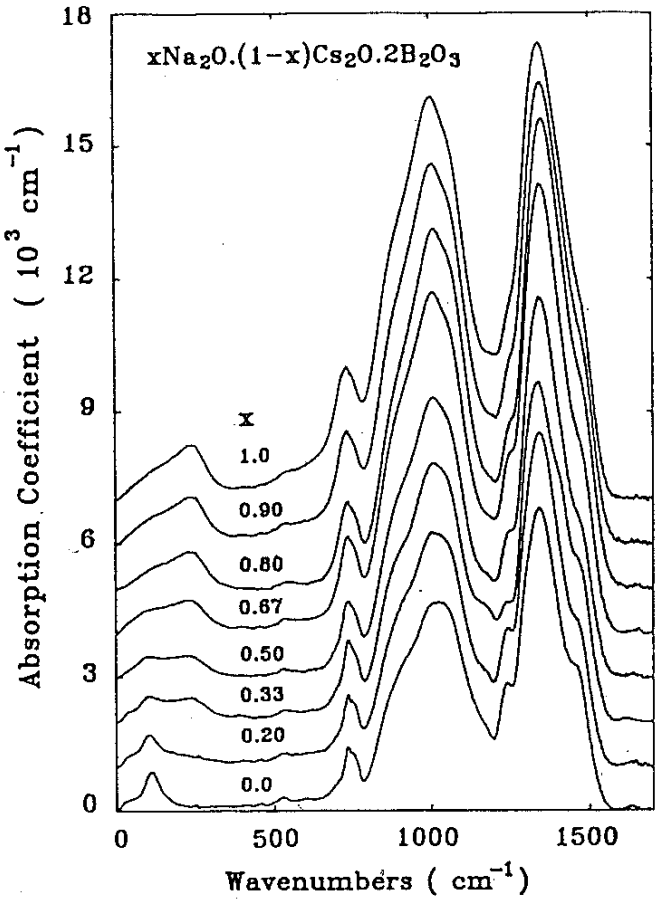

Figure 1. *Infrared absorption spectra of mixed alkali glasses $xNa_2O.(1-x)Cs_2O.2B_2O_3$*

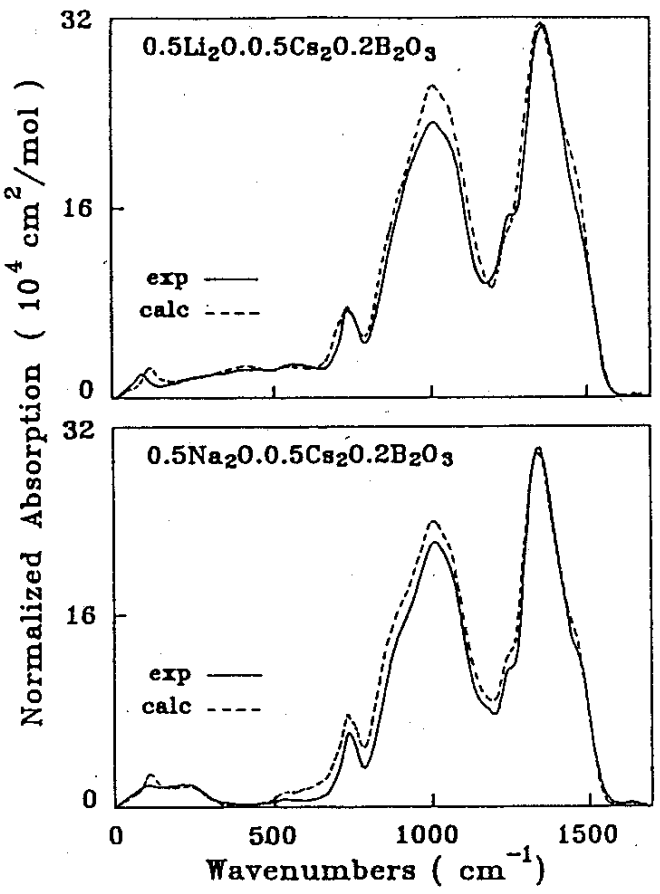

Figure 2. *Comparison of experimental and calculated infrared spectra of mixed Li-Cs and Na-Cs diborate glasses at maximum mixing.*

system $xNa_2O.(1-x)Cs_2O.2B_2O_3$. It is obvious that a progressive replacement of one alkali by another results in a systematic variation of the infrared spectrum. It is of interest to investigate whether such spectral variations with x could result from a linear change of the glass structure with alkali substitution. For this purpose we compare in Fig. 2 the experimental infrared spectra of two MAG's, i.e. Li-Cs and Na-Cs of maximum mixing (x = 0.5), with those calculated on the basis of a linear average of the spectra of the two end-member glasses (x = 0, 1). It is noted that spectral normalization was performed before averaging, by multiplying the absorption coefficient with the glass molar volume, in order to take into account differences in glass density (11, 12). The molar volume of the mixed alkali glass was estimated from the average of the molar volumes of the end-members (1).

Comparison of experimental and calculated spectra in Fig. 2 shows that there is no matching in the various spectral regions. This immediately suggests that, in principle, the structure of a mixed alkali glass can not be described by a linear combination of the structures of the end-member glasses. Of particular interest is the behaviour of the asymmetric absorption band centered at ca 1000 cm^{-1}, which can be attributed to B-O stretching vibration of borate groups containing $B\emptyset_4^-$ tetrahedra ($\emptyset$=bridging oxygen atom) (10-12). Clearly, absorption of the experimental spectrum in this spectral range is less than that predicted on the basis of a linear variation of the glass structure with x.

To quantify this effect we have evaluated the area under the 800-1100 cm^{-1} absorption band of the experimental spectra and normalized it by multiplying with the corresponding

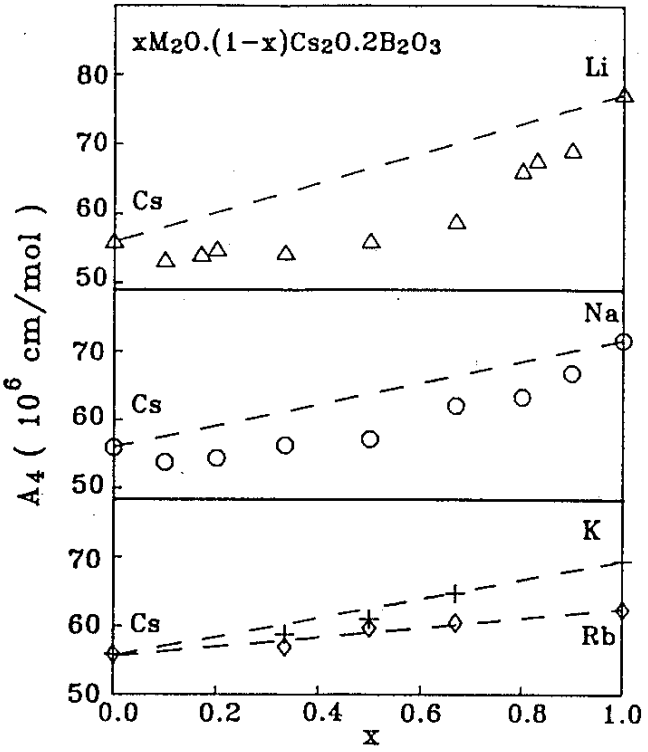

Figure 3. *Normalized infrared area of the 800 - 1100 cm^{-1} spectral region of $xM_2O.(1-x)Cs_2O.2B_2O_3$ glasses.*

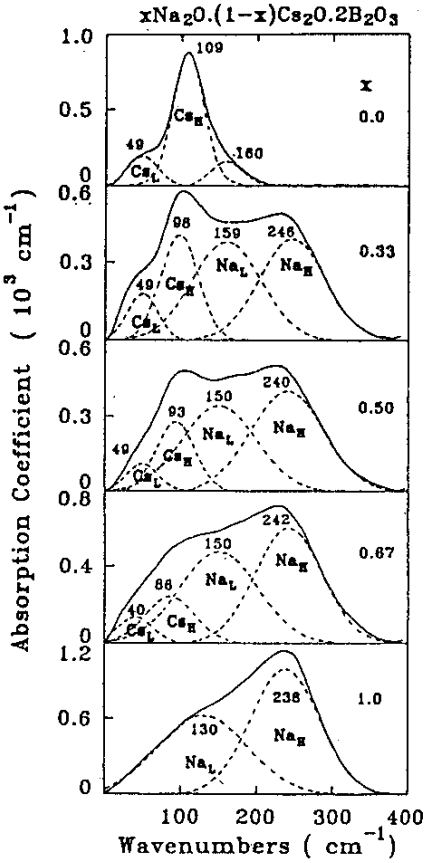

Figure 4. *Deconvoluted far-infrared spectra of $xNa_2O.(1-x)Cs_2O.2B_2O_3$ glasses.*

molar volume. The so-obtained normalized areas, A_4, have been plotted versus x in Fig. 3, for glasses in the mixed alkali systems $xM_2O.(1-x)Cs_2O.2B_2O_3$, (M = Li, Na, K, Rb). An interesting non-linear dependence of A_4 on x has been obtained for Li-Cs and Na-Cs systems, demonstrating the non-linear change of the structure of mixed alkali glasses with alkali substitution. This effect tends to be reduced as the difference between the dissimilar alkalis becomes smaller (e.g. the K-Cs and Rb-Cs systems). It was recently shown that the normalized area A_4 scales linearly with the fraction of four-coordinated boron atoms N_4 (11). Therefore, Fig. 3 illustrates a reduction of N_4 from additivity upon alkali mixing, in agreement with the NMR results of Zhong and Bray for mixed alkali diborate glasses with x = 0.5 (15). Since for $0<x\leq1$ the total alkali content remains fixed, the plots in Fig. 3 suggest that the fraction of non-bridging oxygens in $B\emptyset_2O^-$ triangles should exhibit a positive departure from linearity with alkali mixing.

3.2 Alkali Sites in Mixed Alkali Glasses

While the vibrations of the glass network are observed mainly in the mid-infrared, the far-infrared parts of the spectra (below *ca* 400 cm^{-1}) are dominated by bands attributed to vibrations of alkali cations in their localized network sites (9-13). The Fig. 4 shows the far-infrared parts of spectra in the Na-Cs system. Previous studies on single alkali glasses have shown that their far - infrared profiles can be deconvoluted into two component bands, designated by Na_L, Na_H (x=1) and Cs_L, Cs_H (x=0) in Fig. 4. Such bands have been attributed to vibrations of alkali ions in two distinct types of ionic site (9-13), which differ mainly in their local optical basicity (14). Note that the band at 160 cm^{-1} of the Cs-glass (see Fig. 4, x=0) has been attributed to libration modes of disconnected segments of the borate network, such

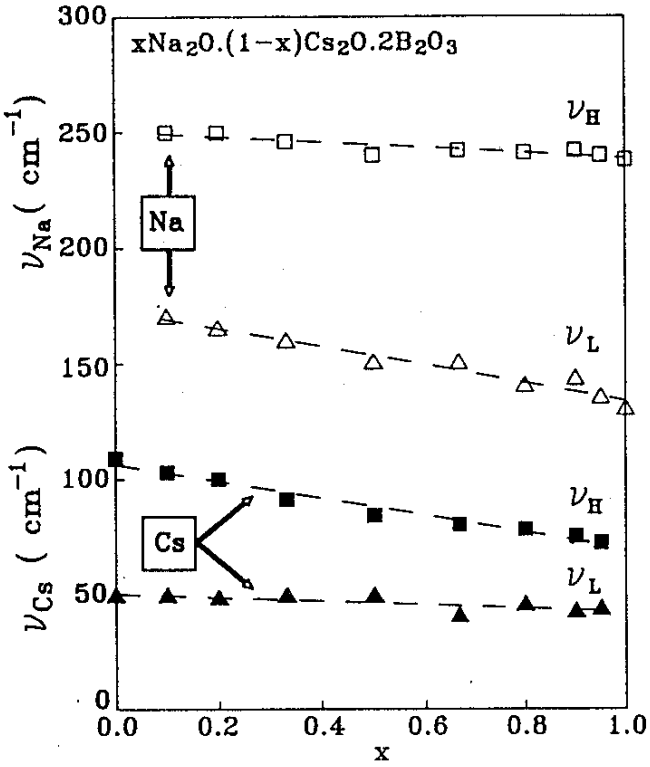

Figure 5. *Sodium and caesium cation-motion frequencies in $xNa_2O.(1-x)Cs_2O.2B_2O_3$ glasses.*

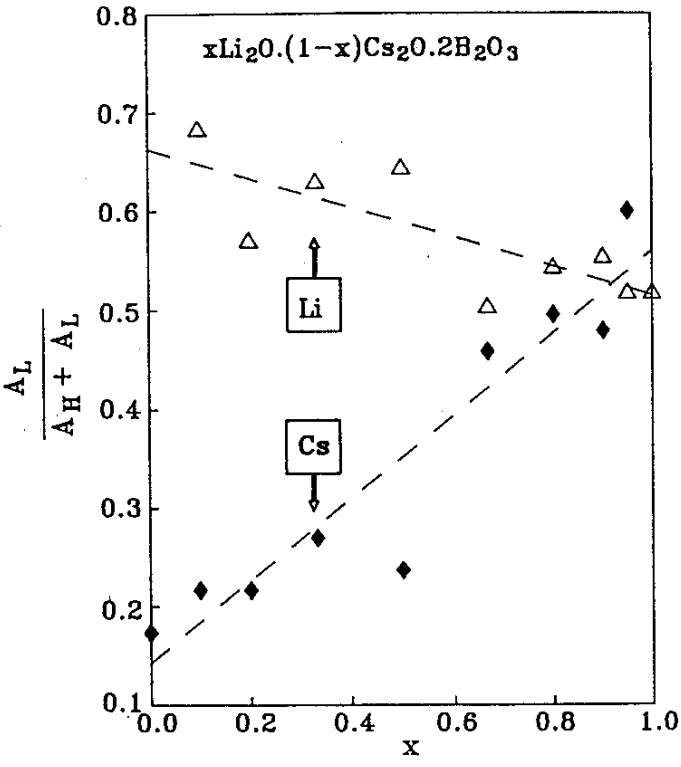

Figure 6. *Relative integrated intensity of the low-frequency ion-motion bands (A_L/A_H+A_L) for Li^+ and Cs^+ ions in $xLi_2O.(1-x)Cs_2O.2B_2O_3$ glasses.*

as those of metaborate rings (11).

Analysis of the far-infrared spectra of mixed alkali glasses has shown that a meaningful simulation requires the consideration of at least four component bands (9). For the particular case shown in Fig. 4, the two bands at lower frequency (ca 50 and 100 cm^{-1}) can be assigned to vibration of Cs cations in their sites, while the two higher frequency components (ca 150 and 240 cm^{-1}) can be attributed to vibrations of Na cations in their suitable sites. Comparison with the spectra of the x=0 and x=1 glasses suggests that the two alkalis occupy sites which are not drastically different from their sites in the single alkali glass. Further knowledge about the nature of such sites in MAG's can be gained by examining the composition dependence of the frequencies of the Na^+- and Cs^+- motion bands. This is shown in Fig. 5, where ν_H and ν_L denote high- and low- frequency components, respectively. It is clear that the Cs^+-motion frequencies, and in particular ν_H, decrease upon decreasing the amount of Cs in the glass. This is in contrast with the behaviour of the Na^+-motion frequencies, particularly that of ν_L, which upshift with decreasing the Na content. The results in Fig. 5 are quite interesting since they demonstrate that for a particular alkali the nature of sites and consequently the cation-site interactions are progressively influenced by the presence of a dissimilar cation. Specifically, the alkali - oxygen attractive forces of the high field strength cation (e.g. Na^+) become stronger, while those of its low field strength partner (e.g. Cs^+) become weaker upon alkali mixing. This clear influence of one alkali on the other can be effected only by their close proximity in network-mediated "pair" configurations. This results in changes of the individual bonding conditions (manifested by ν_H, ν_L) through polarization effects (16,17), as compared to their favoured ones assumed in the binary glass. As shown in the previous section, the glass network responds to fulfil the new bonding requirements by suitable rearrangements like the transformation of $B\emptyset_4^-$ tetrahedra into their

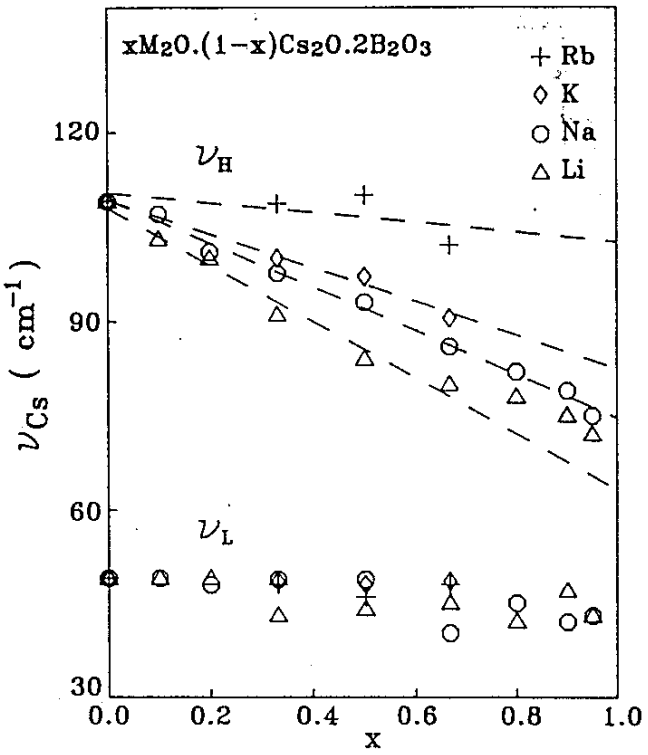

Figure 7. *Cs^+ - motion frequencies in $xM_2O.(1-x)Cs_2O.2B_2O_3$ glasses.*

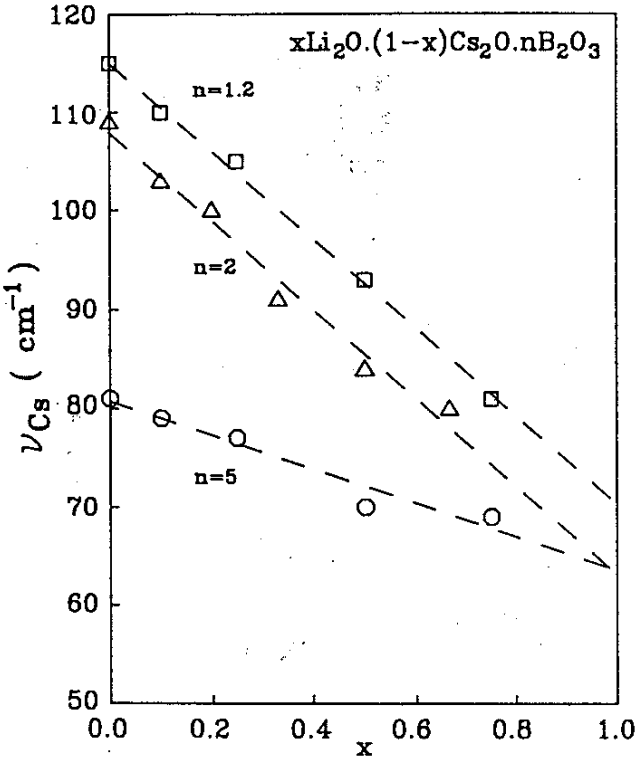

Figure 8. *Effect of total alkali content on the ν_H frequency of Cs^+- motion in $xLi_2O.(1-x)Cs_2O.nB_2O_3$ glasses (n=5, 2, 1.2).*

isomeric $B\emptyset_2O^-$ triangles. Recent EXAFS and molecular dynamics simulation studies of mixed alkali silicate glasses have shown also that the two alkalis affect each other's atomic environment (18, 19).

Besides the observed frequency variations (Fig. 5), a change in the distribution of each alkali ion between its two types of site is also effected upon alkali mixing. As seen in Fig. 4, the two lower-frequency bands (Cs_L, Na_L) gain intensity relative to their higher-frequency counterparts (Cs_H, Na_H), when the two alkalis coexist ($0\langle x\langle 1.0$). The same trend is demonstrated also in Fig. 6 where the relative integrated intensity of the low-frequency component ion-motion bands, $A_L/(A_H + A_L)$, is plotted versus x for glasses in the system $xLi_2O.(1-x)Cs_2O.2B_2O_3$. It is shown that minority cations in mixed-alkali glasses populate preferably the low-frequency sites. We consider this to be an important result, in view of the recent findings in sodium-borate glasses which indicate that the mobile Na^+ ions are those in high-frequency sites (14). Therefore, increase of the population of lower-frequency sites would create discontinuities in the pathways along the higher-frequency sites, with a consequent reduction in ionic conductivity. These structural aspects could be employed as a basis for a better understanding of the mixed alkali effect, as will be discussed in more details elsewhere (20).

3.3. Factors Affecting the Interactions Between Dissimillar Alkalis

The interactions between the dissimilar alkalis were found to depend on their field strength difference. This is demonstrated in Fig. 7 where the variation of the Cs^+-motion frequencies is utilized as a convenient probe of such interactions. It is shown that the larger the difference between the alkali partners (M-Cs) the larger the decrease of the ν_H frequencies of Cs cations, and thus the greater the weakening of the Cs - oxygen interactions. The ν_L frequency shows a much smaller dependence on either M or x.

The effect of the total alkali content on the interactions between alkali cations has been also examined. Preliminary results are presented in Fig. 8 for MAG's in the system $xLi_2O.(1-x)Cs_2O.nB_2O_3$ where n = 5, 2, 1.2. Clearly, the higher the total alkali content the more effective the drop of the ν_H frequency of Cs^+ with Li^+ substitution. This result suggests that for higher total alkali contents there is a greater probability of finding dissimilar alkalis in neighbouring network sites. A full report on such effects in mixed alkali borate and silicate glasses will be reported elsewhere (20).

4. CONCLUSIONS

Infrared spectroscopy has been applied to investigate structural aspects of the mixed alkali effect, including the network structure which provide the sites for the alkali ions, as well as the alkali - oxygen and alkali-alkali interactions. It was found that the structure of the glass network varies non-linearly with alkali substitution, as this is manifested by the negative departure from linearity exhibited by the fraction of four-coordinated boron atoms. The frequencies of the alkali motion bands in the far-infrared were found to vary with alkali substitution, suggesting the presence of dissimilar alkalis in "pair" configurations and the existence of strong interactions that affect in different ways the alkali ion - oxygen attractive forces. A preferential population of the low-frequency cation sites was also found upon alkali mixing and was proposed as a basis for understanding the reduction in ionic conductivity.

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