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INFRARED REFLECTANCE INVESTIGATION OF THE STRUCTURE OF MIXED ALKALI GLASSES

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ABSTRACT

Infrared reflectance spectroscopy has been employed to investigate structural aspects of the mixed alkali effect. The results obtained from the study of mixed alkali borate glasses suggest a non-linear variation of the borate network structure with alkali substitution. The existence of interactions between the dissimilar alkalis was also shown through the variation of the alkali ion-oxygen attractive forces upon alkali mixing. These effects appeared enhanced upon increasing the difference between the alkali partners and the total alkali content.

INTRODUCTION

One special problem related to ionic transport in glasses is the well known mixed alkali effect (MAE), which is assosiated mainly with the large non-linear decrease in ionic conductivity upon replacement of one alkali ion by a dissimilar one. Despite the universality of the MAE and the large number of theories proposed for its explanation its origin remains highly controversial (1). A number of such theories have proposed the existence of interactions between the dissimilar alkali cations, which lower their mobility and consequently affect the glass dynamic properties (2-6). The key point of the relevant theories is the formation of network mediated "pairs" of unlike alkalis, which are energetically favoured compared to "pairs" of similar alkalis. It is reasonable to expect that the formation of "pairs" of dissimilar alkalis will affect their local bonding through polarization effects (7,8), while the glass network will probably readjust to some extent its structure in order to satisfy the new bonding requirements imposed by the presence of dissimilar alkalis in neighbouring network sites. Such phenomena are expected to be manifested by variations in the interactions between alkali cations and their network sites, as well as by alterations of the local structures assumed by the glass network. An effective monitoring of such changes, induced by alkali substitution, can be achieved by applying infrared spectroscopy, as it was recently demonstrated in a preliminary study of mixed alkali glasses (9).

In this report we present an infrared reflectance investigation of the structure 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), in an attempt to contribute towards a better understanding of the MAE. Fourier-transform infrared reflectance spectra have been recorded over a broad frequency range and analysed in order to

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investigate the dependence of the glass structure on the alkali substitution ratio (x), the difference between dissimilar alkalis (M,M') and the total alkali content $(1/(1+n))$. The results have been discussed in light of those obtained by other spectroscopic techniques in relevant mixed alkali glass systems.

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 analysis can be found elsewhere (10).

RESULTS AND DISCUSSION

The Network Structure of Mixed Alkali Borate Glasses

Typical infrared absorption coefficient spectra are shown in Figure 1 for MAG's in the 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, suggesting similar structural changes. 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 Figure 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

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

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 Figure 2 shows that there is no matching in the various spectral regions. This immediately suggests that, in principle, the structure
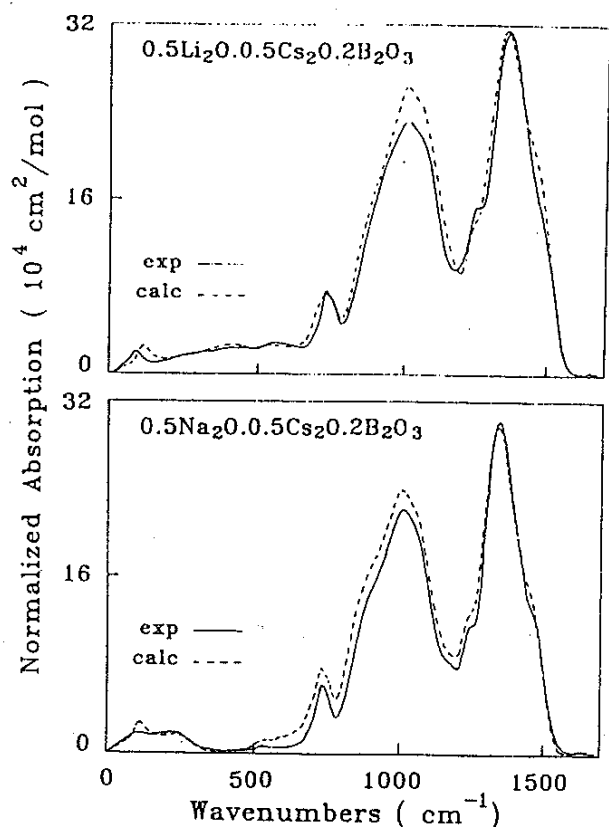
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Figure 2. *Comparison of infrared spectra of mixed Li-Cs and Na-Cs diborate glasses at maximum mixing.*
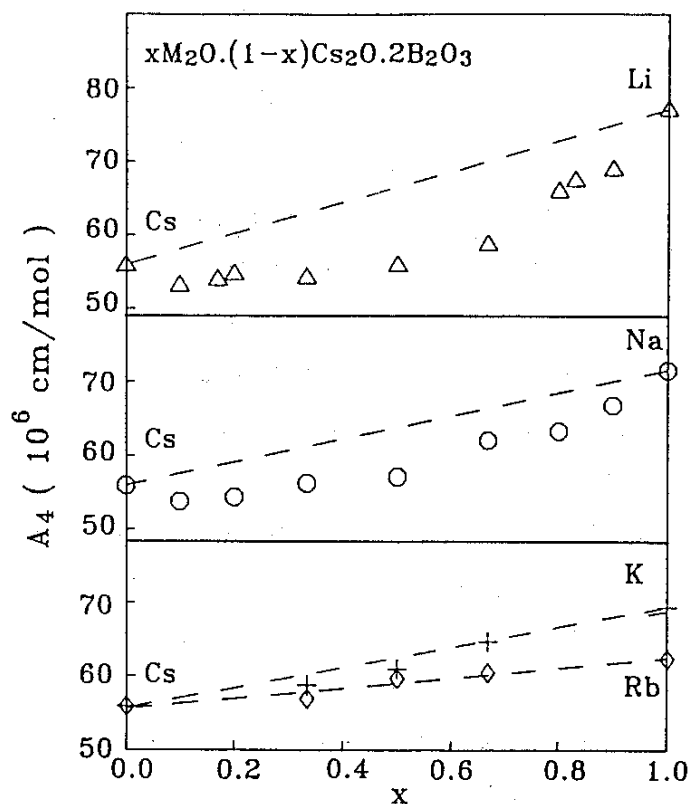
Figure 3. *Normalized infrared area of the 800-1100 cm^{-1} spectral region of $xM_2O.(1-x)Cs_2O.2B_2O_3$ glasses.*

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 BO_4 tetrahedra (10-12). Clearly, the 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 800-1000 cm^{-1} absorption band of the experimental spectra and normalized it by multiplying with the corresponding molar volume. The so-obtained normalized areas, A_4, have been plotted versus x in Figure 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). Since it was recently shown that the normalized area A_4 scales linearly with the fraction of four-coordinated boron atoms N_4 (11), Figure 3 illustrates a reduction of N_4 from additivity upon alkali mixing. This is in agreement with the NMR results of Zhong and Bray for mixed alkali diborate glasses with x=0.5 (13). In addition, the plots in Fig. 3 suggest that the fraction of non-bridging oxygens should exhibit a positive departure from linearity with alkali mixing, considering the fact that the total alkali content remains fixed.

Cation - Network Interactions in Mixed Alkali Borate 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 (9-12). The inset of Figure 1 shows the far-infrared parts of spectra in the Na-Cs system. Previous studies on single alkali glasses (x=0,1) have shown that their far-infrared profiles can be deconvoluted into two component bands, attributed to vibrations of alkali ions in two distributions of ionic site environments (9-12,14). Note that the band at 160 cm^{-1} of the Cs-glass spectrum (see inset of Fig.1) has been attributed to libration modes of disconnected segments of the borate network, such as those of metaborate rings (11).

Figure 4. Sodium and caesium cation-motion frequencies in $xNa_2O.(1-x)Cs_2O.2B_2O_3$ glasses.

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. 1, the two bands at lower frequency (ca 50 and 100 cm^{-1}) can be assigned to vibrations of Cs cations, while the two higher frequency components (ca 150-160 and 240 cm^{-1}) can be attributed to vibrations of Na cations in their suitable network sites. The composition dependence of the frequencies of the Na$^+$- and Cs$^+$- motion bands is shown in Figure 4, where v_H and v_L denote high- and low- frequency components, respectively. It is shown that the Cs$^+$-motion frequencies, and in particular v_H, decrease upon decreasing the amount of Cs in the glass. This is to contrast the behaviour of the Na$^+$-motion frequencies, particularly that of v_L, which upshift with decreasing the Na content. The results of Fig.4 are quite important since they demonstrate that the interactions between alkali cations and their sites are 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. These results contradict those of earlier studies on mixed alkali phosphate (15) and silicate glasses (16).

The interactions between the dissimilar alkalis were found to depend on their field strength difference. This is shown in Figure 5 where the Cs$^+$-motion frequencies are utilized as convenient probes of such interactions. The plots in this figure demonstrate that the larger the difference between the alkali partners the larger the decrease of the v_H frequencies of Cs cations, and thus
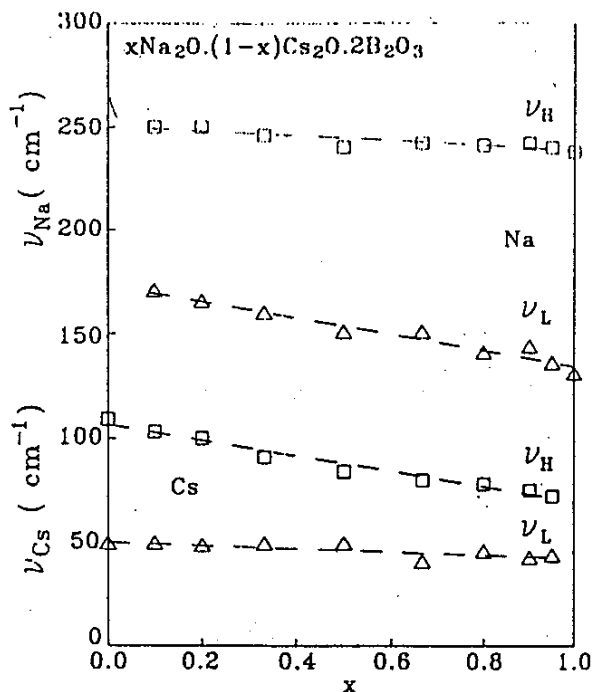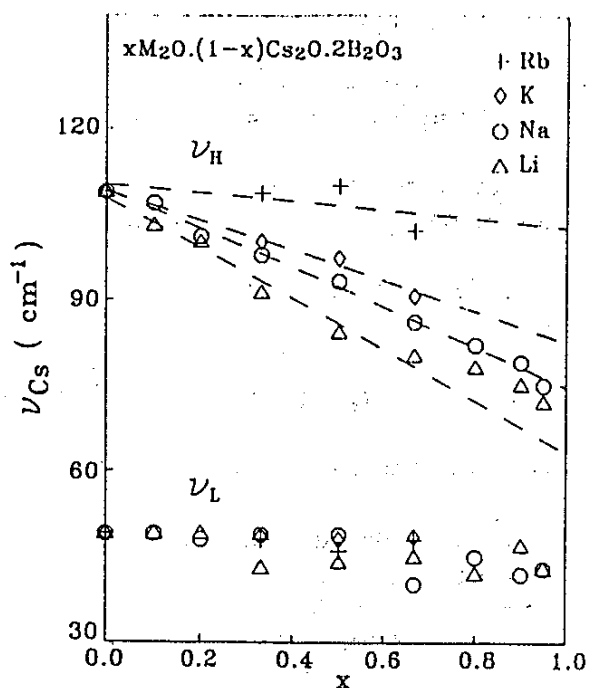
Figure 5. Cs^+-motion frequencies in $xM_2O.(1-x)Cs_2O.2B_2O_3$ glasses.
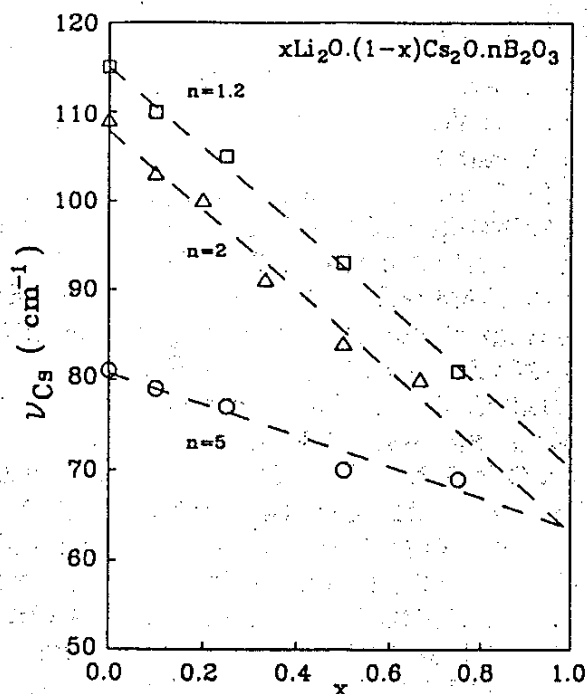
Figure 6. Effect of total alkali content on the v_H frequency of Cs^+-motion in $xLi_2O.(1-x)Cs_2O.nB_2O_3$ glasses $(n = 5, 2, 1.2)$.

the greater the weakening of the Cs-oxygen interactions. The v_L frequency shows a much smaller dependence on either M or x.

The effect of the total alkali content on the interactions between M and M' cations has been also examined. Preliminary results are presented in Figure 6 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 Cs^+ v_H frequency with Li substitution. This result suggests that in MAG's of higher alkali content 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 (17).

CONCLUSIONS

Infrared spectroscopy has been applied to investigate the network structure as well as the alkali-oxygen interactions in mixed alkali borate glasses. 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.

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