

The Physics of Non-Crystalline Solids

Edited by

L. David Pye

W. C. La Course

H. J. Stevens

The Society of Glass Technology



Taylor & Francis

London • Washington DC

1992

INFRARED REFLECTANCE SPECTRA OF MIXED ALKALI BORATE GLASSES

E.I. Kamitsos, A.P. Patsis and G.D. Chryssikos

Theoretical and Physical Chemistry Institute,
National Hellenic Research Foundation,
48 Vass. Constantinou Ave., Athens 116 35, Greece

Infrared reflectance spectra of mixed alkali diborate glasses have been measured and analysed. It was found that alkali substitution results in a non-linear variation of the network structure. The frequencies and intensities of the alkali motion bands in the far-infrared were also found to vary with composition. The spectroscopic results indicate the existence of interactions between the dissimilar alkalis.

INTRODUCTION

The potential of infrared spectroscopy for the structural investigation of glasses has been well documented (Wong and Angell 1976). In particular, infrared measurements of ionic oxide glasses give a direct measure of the interactions between metal cations and their ionic sites, through intense bands in the far-infrared (Exarhos 1986). Higher frequency features observed mainly in the mid-infrared are characteristic of the vibrations of the glass network, and can be employed to probe structural variations with composition.

The application of infrared spectroscopy to the study of mixed alkali glasses is of particular interest considering the limited knowledge of the structure of such complicated systems (Isard 1969, Day 1976, Ingram 1987). A number of theories on the well known mixed alkali effect have proposed the existence of interactions between dissimilar alkali cations which lowers their mobility, and consequently affects strongly the glass dynamic properties (Mazurin 1965, Sakurai and Oaka 1968, Hendrickson and Bray 1972, Ingram 1980, Ingram et al 1980, Dietzel 1983, Waesche and Brückner 1989, Kahnt and Reau 1990). Such interactions are assumed to lead to the formation of network-mediated "pairs" of unlike alkalis, which are energetically more favoured compared to "pairs" of similar alkali ions.

Formation of pairs of dissimilar alkalis will naturally affect the local bonding characteristics through polarization effects, while the glass network has to readjust its structure in order to satisfy the new bonding/coordination requirements imposed by the presence of neighbouring dissimilar alkalis. Such effects are expected to be manifested by variations in both the cation-site interactions, as well as the network structure, and thus can be monitored by infrared spectroscopy.

In this paper we report infrared spectroscopic results on mixed alkali diborate glasses. A parallel study of single alkali diborate glasses is also presented in order to assist the identification of spectral features characteristic of the presence of dissimilar alkalis.

EXPERIMENTAL

Binary $M_2O \cdot 2B_2O_3$ and mixed alkali glasses $xM_2O \cdot (1-x)M'_2O \cdot 2B_2O_3$ ($M, M' = \text{alkali}$) were prepared from the stoichiometric amounts of metal carbonates and B_2O_3 . The batch mixtures were melted in platinum crucibles at $900\text{--}1200^\circ\text{C}$ for about 10–30 min depending of composition. Glass samples with good surfaces were obtained by quenching the melt between two pre-heated copper blocks, and were used for infrared measurements without further treatment.

Infrared spectra were measured in the reflectance mode to avoid spectral distortions, which are frequently observed in transmission measurements. A Bruker 113 v spectrometer, equipped with the appropriate reflectance attachment, sources, detectors and beam splitters, was used for recording continuous reflectance spectra in the range $30\text{--}4,000\text{ cm}^{-1}$. The so obtained reflectance data were transformed by Kramers-Kronig inversion to yield the absorption spectra reported in this work. Experimental details regarding sample preparation and data analysis have been reported elsewhere (Kamitsos et al 1990, Kamitsos et al 1991).

RESULTS AND DISCUSSION

Infrared Spectra of Single Alkali Glasses

The infrared spectra of alkali diborate glasses are presented in Figure 1 in the form of absorption coefficient spectra. All spectra, except that of the Cs-glass, have been off-setted to facilitate comparison. It is observed that both the overall spectral profiles and their absolute intensities depend strongly on the modifying alkali cation.

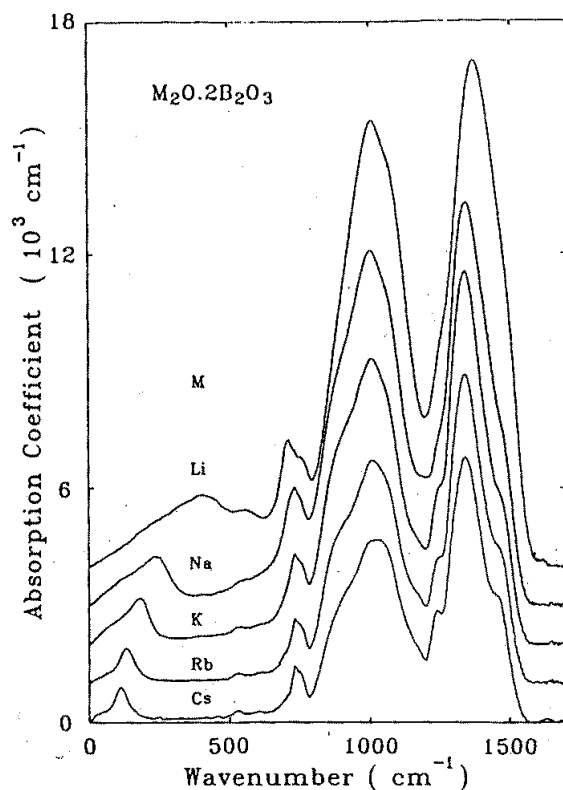


Figure 1. Infrared spectra of single alkali borate glasses $M_2O \cdot 2B_2O_3$.

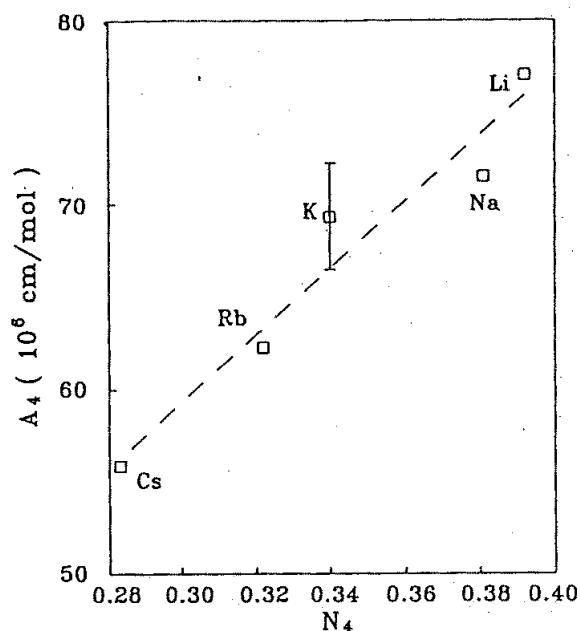


Figure 2. Normalized infrared area, A_4 , of the $800\text{--}1180\text{ cm}^{-1}$ spectral region of $M_2O \cdot 2B_2O_3$ glasses versus the fraction of four coordinated boron atoms, N_4 .

The far-infrared region (below 500 cm^{-1}) is dominated by a clearly asymmetric band, whose frequency at peak maximum shifts to higher values upon decreasing cation mass. Such far-infrared bands of ionic glasses have been assigned to vibrations of metal cations in their localized sites in the glass (Exarhos and Risen 1972). The cation-motion frequency has been recently evaluated in terms of the cation and anionic site charges, the reduced mass of cation vibration and the metal ion-oxygen distance (Kamitsos 1989). A systematic deconvolution of the asymmetric cation-motion bands has revealed the presence of two Gaussian type components (Kamitsos et al 1991), which are assigned to vibrations of alkali cations in two different distributions of anion site environments (Kamitsos et al 1987).

The mid-infrared features of the spectra can be generally discussed in terms of vibrations of various network forming groups. Of particular interest is the range of the spectrum between $800\text{--}1200\text{ cm}^{-1}$, in which absorption originates from stretching vibrations of BO_4 tetrahedral units (Krogh-Moe 1965). The complex band in this spectral region is indicative of overlapping contributions from a number of bands, suggesting the presence of BO_4 tetrahedra in different types of borate arrangements. Obviously, the changing shape and intensity of this envelope with M shows the influence of the alkali cation on the glass network structure.

In an attempt to quantify this effect we have measured the area under the $800\text{--}1180\text{ cm}^{-1}$ absorption band, and normalized it by multiplying with the corresponding molar volume (Chong et al 1989) to account for differences in glass density. Figure 2 shows the normalized infrared area attributed to BO_4 tetrahedra as a function of N_4 , the fraction of four-coordinated boron atoms obtained recently from NMR data (Zhong and Bray 1989). The two data sets are related quite linearly. Thus, the fraction of four-coordinated boron atoms decreases systematically upon increasing cation size, while the opposite trend is inferred for three coordinated boron atoms bonded to non-bridging oxygens. Such results contradict the earlier belief that the structure of borate glasses is solely a function of the alkali oxide content.

Infrared Spectra of Mixed Alkali Glasses

Mixed alkali diborate glasses have been prepared for various combination of alkalis M and M' and their spectra have been measured. Typical spectra are shown in Figure 3 for glasses in the system Li-Cs. Clearly, the progressive replacement of one alkali by the other results in the systematic variation of glass structure. To further investigate the details of the structural variation with alkali substitution, we have obtained the normalized infrared areas ($800\text{--}1180\text{ cm}^{-1}$) and plotted them versus x in Figure 4. Molar volumes of mixed alkali glasses were calculated on the basis of those of the binary glasses ($x=0,1$) assuming a linear variation with x (Isard 1969, Day 1976, Ingram 1987). Figure 4 demonstrates an interesting non-linear variation of mixed alkali glass structure with composition. Specifically, the concentration of BO_4 tetrahedra-containing groups shows a negative departure from linearity upon alkali mixing, suggesting the opposite trend for the non-bridging oxygen-containing structural groups. The same trend has been observed for all mixed alkali borate glasses studied, though the magnitude of the departure from additivity was found to decrease upon decreasing the difference in size of the dissimilar alkalis (Kamitsos et al 1991). A similar reduction of N_4 compared to that expected from linearity, has been found also from the analysis of the NMR spectra of mixed alkali diborate glasses with $x=0.5$ (Zhong and Bray 1989).

Additional spectral trends can be obtained by considering the far-infrared part of the spectra in Figure 3. It is observed that the intensity of the Cs-motion band decreases upon increasing x, and is accompanied by a

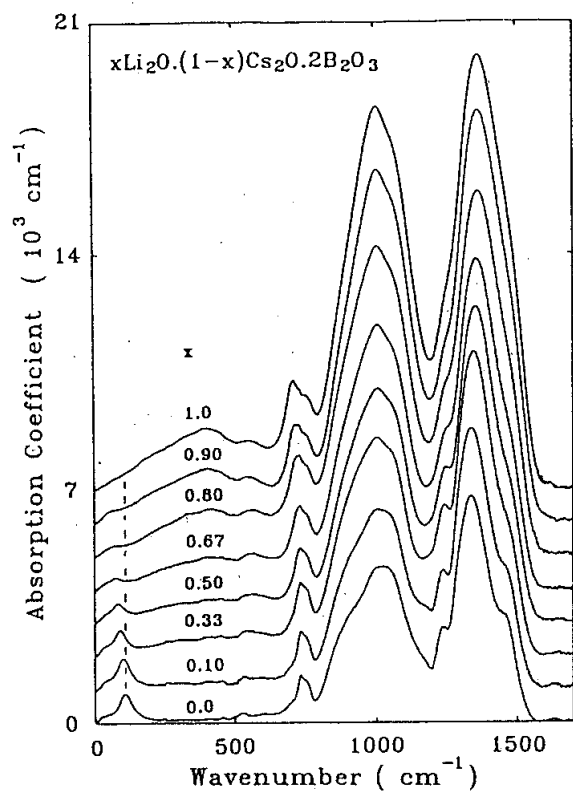


Figure 3. Infrared spectra of mixed alkali borate glasses $x\text{Li}_2\text{O} \cdot (1-x)\text{Cs}_2\text{O} \cdot 2\text{B}_2\text{O}_3$.

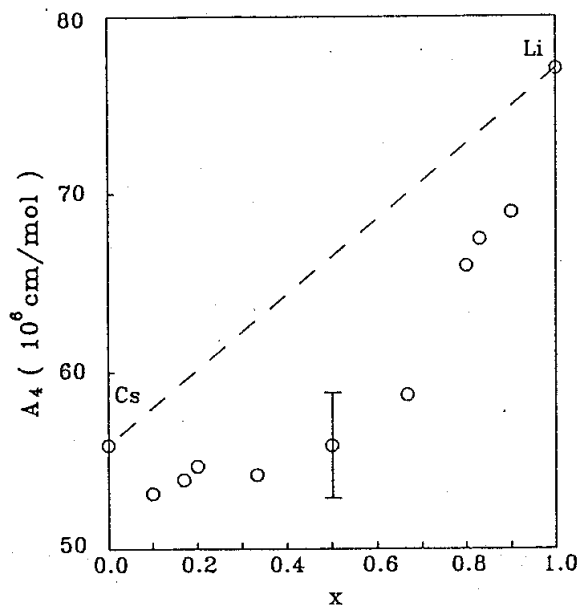


Figure 4. Composition dependence of the normalized infrared area of the $800\text{--}1180\text{ cm}^{-1}$ spectral region of $x\text{Li}_2\text{O} \cdot (1-x)\text{Cs}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glasses.

parallel decrease in peak frequency (ca 100 cm^{-1} for $x=0$). While the intensity variation is consistent with the concentration of Cs cations in the glass, the obtained Cs frequency shift presents a new important result. This is mainly because earlier findings in mixed alkali phosphate and silicate glasses had indicated that the cation motion frequency was independent of x (Rouse et al 1978, Kamitsos and Risen 1984, Minser and White 1984). These results had been interpreted as suggesting that the dissimilar alkalis do not influence each other.

The observed decrease of the Cs-motion frequency with Li substitution suggests that indeed the Cs-O interactions are affected by Li cations, and that they become weaker than those in the binary glass ($x=0$). A similar examination of the high frequency side of the far-infrared spectra, where the Li vibrations are active (ca 400 cm^{-1}), can not give conclusive evidence about a possible dependence of the band maximum on x , due to the large bandwidth of the relevant band. To overcome this difficulty a deconvolution of the whole far-infrared profile is required. Indeed, preliminary results show that the Li motion frequency increases with decreasing x (Kamitsos et al 1991).

A complementary approach to this problem is illustrated in Figure 5, where far-infrared spectra are presented for various mixed alkali glasses of maximum alkali mixing ($x=0.5$). The continuous lines represent the experimental far-infrared spectra, while the dashed ones are linear combinations of the corresponding binary glass spectra all being properly normalized

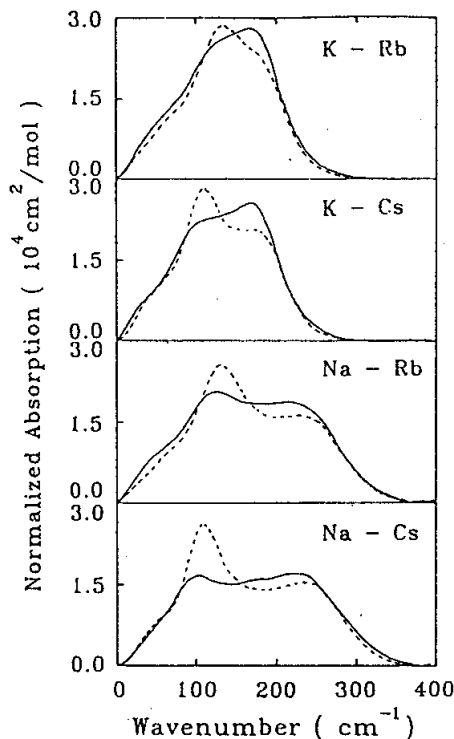


Figure 5. Comparison of experimental (—) and calculated (---) far-infrared spectra of mixed (M-M') diborate glasses of maximum mixing ($x=0.5$).

for density effects. Figure 5 directly shows that the spectrum of a mixed alkali glass can not be simulated by the appropriate average of the two end-member spectra. This is in perfect agreement with the mid-infrared results presented above (Fig.4). In addition, Fig.5 shows that the Cs- and Rb-motion bands in the experimental spectra suffer a frequency, and even more pronounced an intensity decrease, compared to calculated spectra. Contrary to that, the Na- and K-bands gain in frequency and intensity upon alkali mixing. In relation to these results, it is interesting to note that a recent EXAFS study of the KCsSi_2O_5 mixed alkali silicate glass has shown also that the two alkalis affect one another's atomic environment (Greaves 1989).

CONCLUSIONS

The spectral data presented in this work demonstrate that the presence of dissimilar alkalis in diborate glasses has a pronounced effect on their interactions with the glass network. Thus, the ionic interactions of the low-field strength cation (e.g. Cs^+) with their network sites become weaker, while these of the higher-field strength partner (e.g. Li^+) become stronger than those in the corresponding binary glasses. Such a clear influence of one alkali on the other can only be effected by their close proximity in network-mediated "pair" configurations. Due to the difference in polarizing power or field strength of the unlike alkalis, the formation of pairs of dissimilar cations results in changes of their individual bonding conditions, as compared to their "favoured" ones assumed in the binary glasses. The glass network responds to fulfill the new bonding requirements, by transforming BO_4 tetrahedra into their isomeric trigonal borate units with non-bridging oxygens, that render the network higher flexibility for structural rearrangements.

ACKNOWLEDGEMENTS

This work has been supported by NHRF. Stimulating discussions with Dr. M.D. Ingram are gratefully acknowledged.

REFERENCES

- Chong B.C., Choo S.H., Feller S., Teoh B., Mathews O, Khaw E.J., Feil D., Chong K.H. Affatigato M., Bain D., Hazen H. and Farooqui K., 1989, J.Non-Crystalline Solids, 109, 105.
- Day D.E., 1976, J.Non-Crystalline Solids, 21, 343.
- Dietzel A.H., 1983, Phys.Chem.Glasses, 24, 172.
- Exarhos G.J., 1986, in: Structure and Bonding in Non-Crystalline Solids, edited by G.E.Walrafen and A.G.Revesz, (New York:Plenum Press) p.119.
- Exarhos G.J., and Risen W.M., 1972, Solid State Commun., 11, 755.
- Greaves G.N., 1989, Philosophical Magazine B, 60, 795
- Hendrickson J.R. and Bray P.J., 1972, Phys.Chem.Glasses, 13, 43, 107.
- Ingram M.D., 1980, J.Am.Ceram.Soc., 63, 248
- Ingram M.D., 1987, Phys.Chem.Glasses, 28, 215.
- Ingram M.D., Moynihan C.T. and Lesikar A.V., 1980, J.Non-Crystalline Solids, 38-39, 371
- Isard J.O, 1969, J.Non-Crystalline Solids, 1, 235
- Kahnt H. and Reau J.M, 1990, J.Non-Crystalline Solids, 125, 143
- Kamitsos E.I. , 1989, J.Phys.Chem., 93, 1604.
- Kamitsos E.I., and Risen W.M., 1984, J.Non-Crystalline Solids, 65, 333.
- Kamitsos E.I., Karakassides M.A. and Chryssikos G.D., 1987, J.Phys.Chem., 91, 5807.
- Kamitsos E.I., Patsis A.P., Karakassides M.A. and Chryssikos G.D., 1990, J.Non-Crystalline Solids, 126, 52
- Kamitsos E.I., Patsis A.P. and Chryssikos G.D., 1991, Phys.Chem.Glasses, (in press).
- Krogh-Moe J., 1965, Phys. Chem.Glasses, 6, 46.
- Mazurin O.V., 1965, in:The structure of Glass (New York: Consultants Bureau) vol.IV, p.5.
- Minser G.D. and White W.B., 1984, in Spectroscopic Investigations of Glass Structure (U.S.Department of Energy Annual Report) N° DOE/ER/450077-1.
- Sakurai J. and Oaka K., 1968, Toshiba Rev., 23, 913
- Waesche R. and Brückner R., 1989, J.Non-Crystalline Solids, 107, 309.
- Wong J. and Angell C.A., 1976 in Glass Structure by Spectroscopy, (New York: Dekker), p. 409.
- Zhong J. and Bray P.J., 1989, J.Non-Crystalline Solids, 111, 67.