SOLID STATE IONICS

Proceedings of Symposium A2 on
Solid State Ionics
of the International Conference on Advanced Materials – ICAM 91
Strasbourg, France, 27–31 May, 1991

Edited by:

M. BALKANSKI
Laboratoire de Physique des Solides
Université Pierre et Marie Curie
Paris, France

T. TAKAHASHI
Nagoya University
Nagoya, Japan

H.L. TULLER
Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, MA, USA

1992

NORTH-HOLLAND
AMSTERDAM • LONDON • NEW YORK • TOKYO

Solid State Ionics
M. Balkanski, T. Takahashi and H.L. Tuller (Editors)

Structural studies of single and mixed alkali borate glasses

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

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

Abstract

Infrared and Raman spectroscopies have been employed to study the structure of borate glasses. The results presented for single alkali glasses illustrate the strong dependence of the network structure on the nature and content of the oxide modifier. Variations of the cation-motion frequencies in the far-infrared spectra of mixed alkali glasses have been interpreted as suggesting changes in the alkali-oxygen interactions upon alkali mixing.

1. INTRODUCTION

It has been widely recognized that the limited understanding of glass structure presents one of the main obstacles for formulating a generally accepted theory of ion transport in amorphous solids [1,2]. This problem is further complicated when alkali borate glasses are considered, because of their structural peculiarities known as the "boron anomaly effect". Early studies have emphasized the effect of modifier content on the network glass structure [3-5], but provide limited insight into the dependence of the latter on the type of alkali modifier.

The discovery of borate glass compositions with high ionic conductivities has renewed interest in such systems, and thus the elucidation of their structure-property relationships has become a key issue. In this paper we report results of infrared and Raman spectroscopies, with the purpose of probing the evolution of borate glass structure as a function of content and nature of the alkali oxide employed.

The vibrational studies have been extended to mixed alkali borate glasses, which are characterized by pronounced non-linearities in the compositional dependence of their dynamic properties, including electrical conductivity [2,6,7]. Results regarding the effect of mixing dissimilar alkalis on the interactions between cations and network sites are reported.

2. EXPERIMENTAL

Binary $xM_2O.(1-x)B_2O_3$ as well as mixed alkali borate glasses $xM_2O.(1-x)M'_2O.2B_2O_3$ (M, M'=alkali) were prepared from the stoichiometric proportions of metal carbonates and B_2O_3, which were melted in platinum crucibles at 900-1200°C for about 30 min. Fast quenching the melt between two copper blocks resulted in samples with quite good surfaces, which were used directly for spectroscopic measurements.

Raman spectra were measured on a Ramanor HG 2S Jobin-Yvon spectrometer, with 90° scattering geometry and 488 nm excitation. Continuous infrared reflectance spectra in the range 30-4,000 cm^{-1} were obtained on a Bruker 113 v spectrometer, and were transformed by Kramers-Kronig inversion to yield the absorption spectra. Details on sample preparation, handling and spectroscopic measurements can be found elsewhere [8-11].

3. RESULTS AND DISCUSSION

3.1. Evolution of network structure with alkali content.

Glasses in the lithium borate system can be prepared in a continuous and broad glass forming region ($0 \leq x \leq 0.73$). Such glass forming ability, combined with the minimum tendency for carbonate retention in high basicity glasses [12], make the lithium borate system ideal for the investigation of the glass structure over an extensive range of metal oxide contents.

Infrared absorption spectra of compositions spanning the whole accessible glass forming region in the Li-borate system are shown in Figure 1. The mid-infrared part of the spectra (600-1600 cm^{-1}) can be generally discussed in terms of vibrations of various network forming units, as it will be presented below. The far-infrared region (30-600 cm^{-1}) is dominated by a broad and asymmetric absorption envelope, with intensity and frequency at maximum both increasing with Li_2O content. This band has been assigned to vibrations of lithium cations in their network sites, and its asymmetry has been associated with the presence of two broad distributions of anionic site environments [10].

Some key structural points resulting from the consideration of the mid-infrared parts of the spectra are communicated here. The obvious effect of adding Li_2O to B_2O_3 is the growing of a multiple band in the region 800-1200 cm^{-1}, attributed to B-O stretching vibrations of $BØ_4^-$ tetrahedra (Ø=bridging oxygen atom). This absorption envelope gains a maximum relative intensity at about x=0.40 and then it decreases for higher lithium contents. Such a behavior indicates the initial creation of $BØ_4^-$-containing groups and their subsequent destructions in favor of those containing non-bridging oxygen atoms. Units of the latter type are the chain metaborates, $(BØ_2O^-)_n$, as indicated by their characteristic band at 1240 cm^{-1} and the pyroborates, $B_2O_5^{4-}$, (1130 cm^{-1}). In addition, bands at 1300 cm^{-1} ($x>0.50$) and 775 cm^{-1} clearly manifest the formation of orthoborate species, BO_3^{3-} [10].

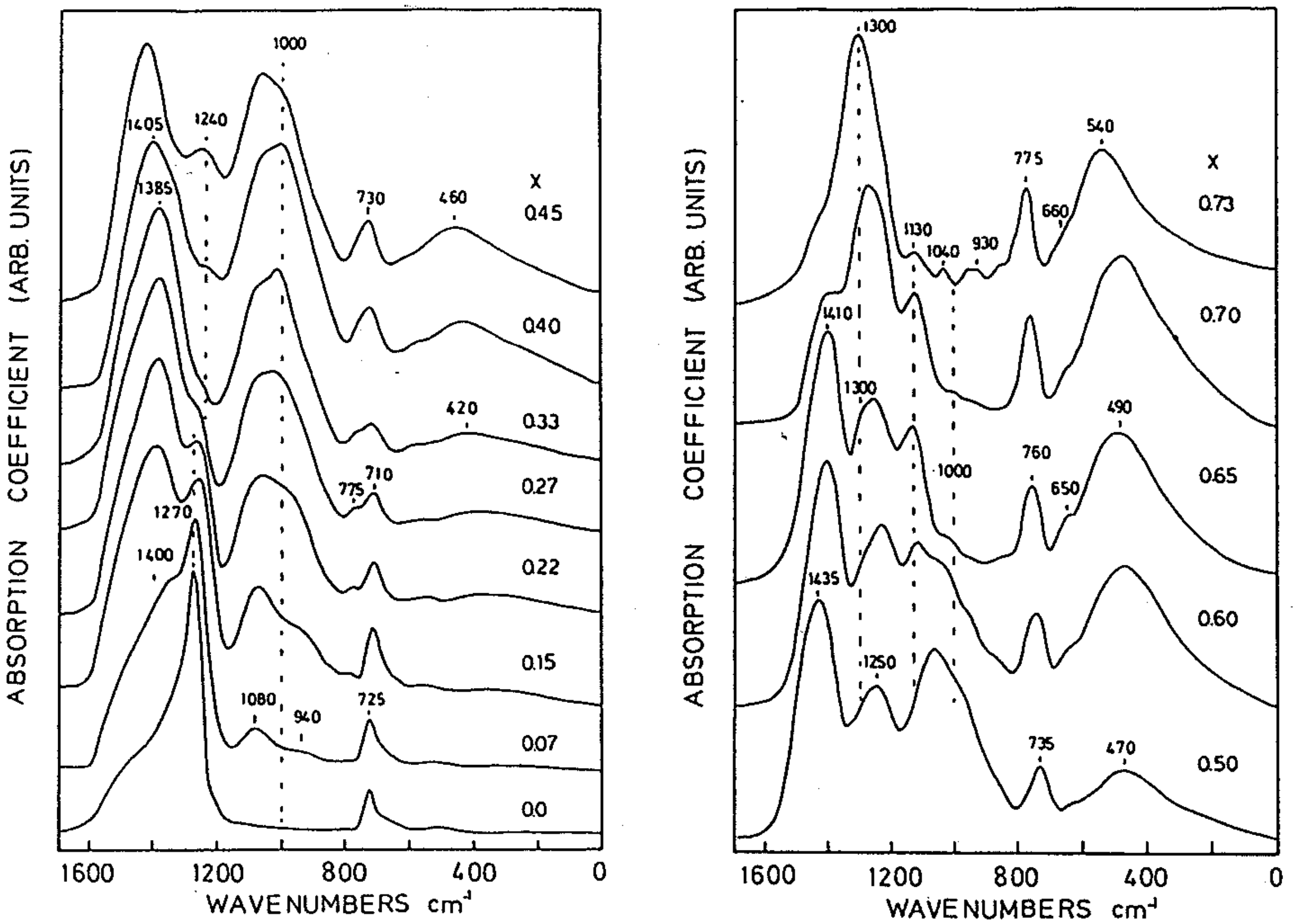

Figure 1. Infrared spectra of $xLi_2O.(1-x)B_2O_3$ glasses

While the detailed study of the infrared spectra has been reported elsewhere [10], Figure 2 presents schematically the network modification process in terms of normalized infrared band areas of characteristic borate units, at various Li_2O contents. Thus, bands attributed to $BØ_4^-$ - containing units are dominating the spectrum at $x=0.40$, while metaborate chains and pyroborate units gain their maximum concentration at $x=0.50$ and $x=0.65$ respectively. Orthoborates are the predominant species in glasses of higher lithium content.

This network modification pattern is in agreement with that deduced from the study of the Raman spectra of Li- and Na-borate glasses [8], but is at variance with the one found for Cs- and Rb-glasses especially at high alkali contents [9]. This issue is examined in the next section.

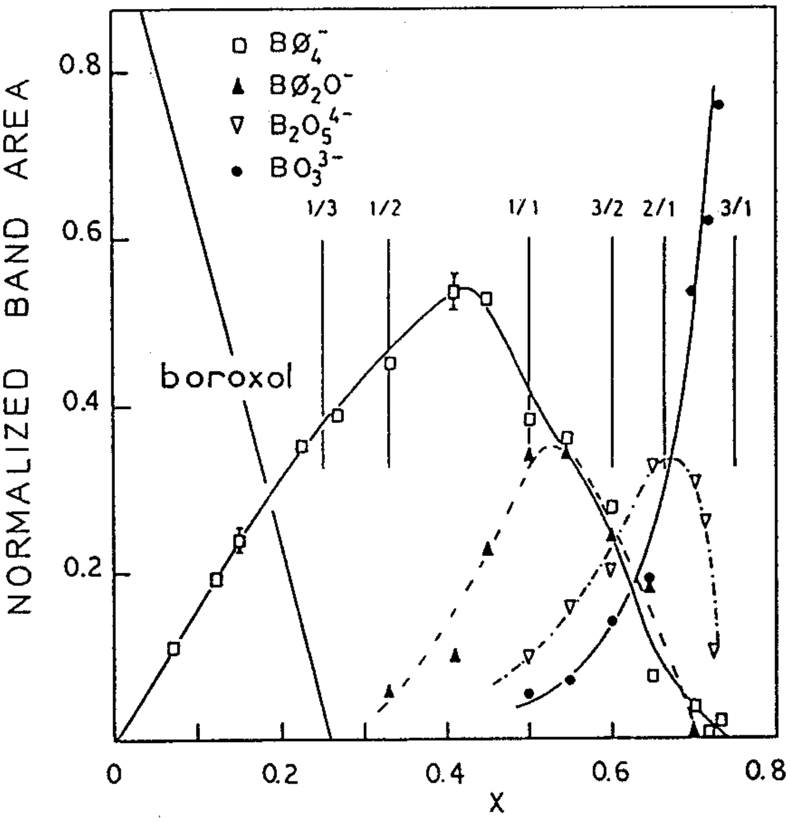

Figure 2. Normalized infrared band areas of borate units found in lithium borate glasses. Vertical lines mark the composition of known lithium borate compounds of various Li_2O/B_2O_3 ratios.

3.2. Dependence of network structure on alkali cation type.

A recent study of the Raman spectra of alkali borate glasses with the same modifier content has revealed distinct differences even at low M_2O contents, illustrating the preference of each alkali to specific borate groups [13]. Such an effect is clearly demonstrated by the spectra of Figure 3 for the x=0.70 composition.

The spectrum of the Li-glass exhibits bands characteristic of orthoborates (925 cm^{-1}), pyroborates (835, 1250 cm^{-1}) and six-membered rings with $BØ_4^-$ tetrahedra (763 cm^{-1}). Bands attributed to similar network building units are also evident in the spectrum of the Na-borate glass. The spectrum of the K-glass shows weak features of orthoborates (865 cm^{-1}), and pyroborates (810 cm^{-1}), as well as metaborate-chains (740 cm^{-1}) and rings (608 cm^{-1}). The strongest bands at 680 and 350 cm^{-1} have been assigned to $BØ_2O_2^{3-}$ units [9]. These tetrahedra contain two bridging and two non-bridging oxygen atoms and are isomeric to orthoborate triangles, BO_3^{3-}. The presence of intense bands at about 675 and 345 cm^{-1} in the spectra of Rb- and Cs-glasses indicates that

$B\varnothing_2O_2^{3-}$ tetrahedra constitute the main network forming units of these glasses.

These structural differences have been employed to account for the unusually high glass transition temperatures of Li-Rb and Li-Cs orthoborate glasses, as opposed to their Li-Na counterpart [14].

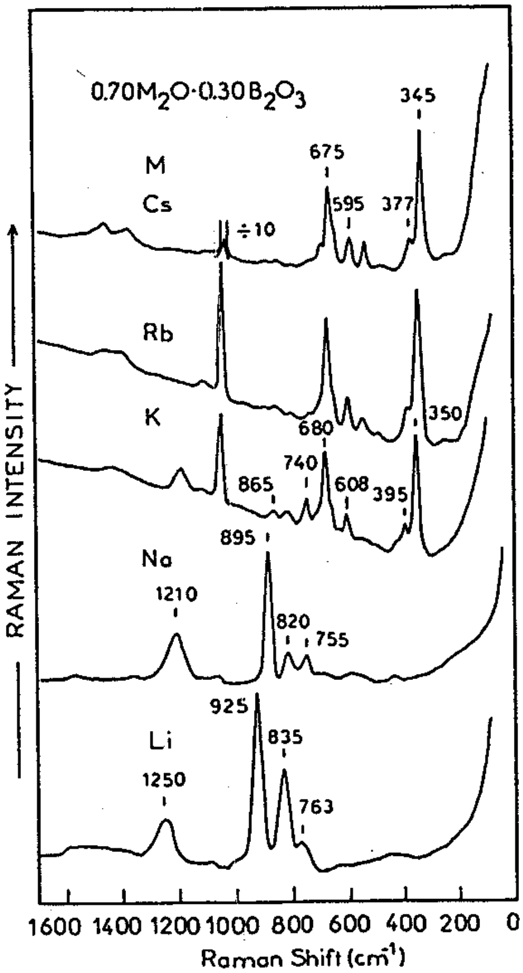

Figure 3. Raman spectra of alkali borate glasses of composition $0.7M_2O.0.3B_2O_3$.

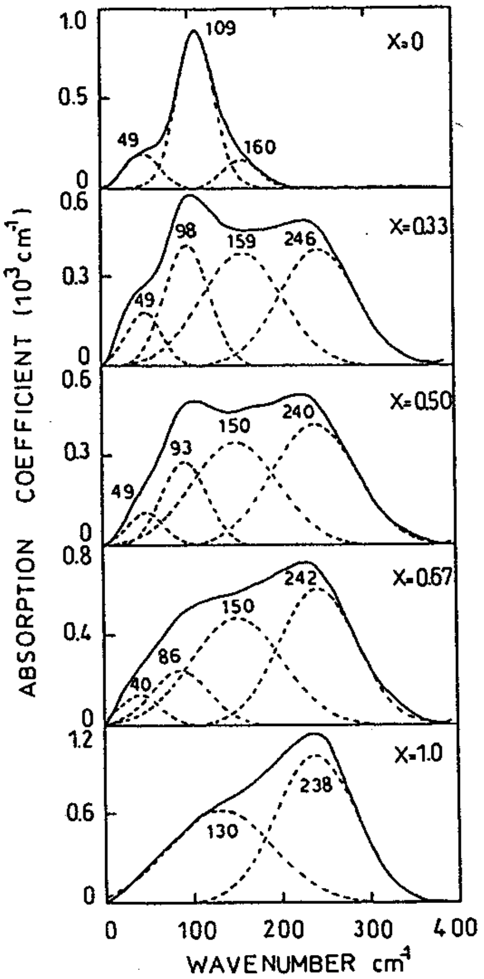

Figure 4. Far-infrared spectra of mixed alkali, $xNa_2O.(1-x)Cs_2O.2B_2O_3$ glasses(continuous lines). Dashed lines indicate the Gaussian components obtained by deconvolution of the measured spectra.

3.3. Cation-network interactions in mixed alkali glasses.

As noted in section 3.1 the vibrations of alkali cations in their network sites are active in the low frequency part of the infrared spectrum. This makes far-infrared spectroscopy a useful probe of the cation-cation and cation-network interactions that may be relevant to the mixed alkali effect [2]. Far-infrared spectra of representative mixed alkali compositions $xNa_2O.(1-x)Cs_2O.2B_2O_3$ are shown in Figure 4 for various values of x.

The spectrum of the binary Na-glass (x=1) has been deconvoluted into two component bands as previously described [11]. These bands are attributed to

Na^+ vibrations in two different distributions of anionic site environments. A similar result applies for the Cs-glass (x=0), since the high frequency feature at 160 cm^{-1} was attributed to hydrolysis effects. Deconvolution of the broad mixed alkali glass spectra (x=0.33, 0.50, 0.67) resulted in at least four component bands. The two lower-frequency ones at about 50 and 100 cm^{-1} are assigned to Cs^+ vibrations and those at about 150-160 and 240 cm^{-1} to Na^+ vibrations in the mixed alkali glass [11].

Consideration of band maxima marked in Figure 4 suggests that the Cs^+ vibration frequencies shift to lower values in mixed alkali glasses, while those of Na^+ cations increase upon alkali mixing. These results demonstrate for the first time that the interactions between alkali cations and glass network are affected by the presence of dissimilar cations. Specifically, the Cs-O interactions become weaker than in the binary glass (x=0), while the Na-O interactions are strengthened in mixed alkali glasses. The Raman and mid-infrared spectra of these and similar glasses have been also studied to investigate the structural reasons that could account for such effects. The non-linear variation of the network structure of mixed alkali glasses was a key result of these studies [11].

4. REFERENCES

1 H.L. Tuller and P.K.Moon, Mater.Sci.Eng. B1 (1988) 171.
2 M.D. Ingram, Phys.Chem.Glasses, 28 (1987) 215.
3 J.Krogh-Moe, Phys.Chem.Glasses, 6 (1965) 46.
4 P.J. Bray and J.O'Keefe, Phys.Chem.Glasses, 4 (1963) 37.
5 W.L. Konijnendijk and J.M.Stevels, J.Non-Cryst. Solids, 18 (1975) 307.
6 J.O.Isard, J.Non-Cryst.Solids, 1 (1969) 235.
7 D.E. Day, J.Non-Cryst. Solids, 21 (1976) 343.
8 E.I. Kamitsos, M.A.Karakassides and G.D.Chryssikos, Phys. Chem. Glasses, 28 (1987) 203 and 30 (1989) 19.
9 G.D.Chryssikos, E.I.Kamitsos, A.P.Patsis and M.A.Karakassides , Mater. Sci.Eng. B7 (1990) 1
10 E.I.Kamitsos, A.P.Patsis , M.A.Karakassides and G.D.Chryssikos, J.Non-Cryst.Solids, 126 (1990) 52
11 E.I. Kamitsos, A.P. Patsis and G.D.Chryssikos, Phys.Chem.Glasses, in press (1991).
12 E.I.Kamitsos, M.A.Karakassides and A.P.Patsis, J.Non-Cryst. Solids, 111 (1989) 252.
13 G.D.Chryssikos, E.I.Kamitsos and M.A.Karakassides, Phys.Chem.Glasses, 31 (1990) 109
14 S. Koritala, K. Farooqui, M. Affatigato, S. Feller, S. Kambeyanda, S. Ghosh, E.I. Kamitsos, G.D. Chryssikos, and A.P.Patsis, J. Non-Cryst. Solids, in press (1991).