Infrared reflectance studies of ionic conductive glasses. Network structure and cation dynamics

E. I. KAMITSOS

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

Résumé. Les résultats des nos études de réflectivité dans l'infra-rouge des verres de borates alcalins simples et mixtes sont répertoriés et discutés dans le contexte de la structure du réseau et des interactions entre les cations alcalins et leur sites dans le verre. En particulier, nous insistons sur la forte influence de la nature du cation alcalin, de la concentration et de la substitution alcaline sur la structure des unités de formation du réseau. Le rôle dominant des ions alcalins ressort aussi par l'analyse de leur bands de vibration qui sont actives dans le lointain infra-rouge. Ainsi, la présence de deux différentes distributions de l'environnement des sites anioniques a été trouvée caractéristique pour les verres de borates alcalins simples. L'analyse spectrale correspondante pour les verres alcalins mixtes a révélé l'existence d'interactions entre les alcalins de nature différente, cette interaction influence fortement les caractéristiques de leur liaisons. Les exigences des nouvelles liaisons, obligent le réseau vitreux à subir les réarrangements nécessaires, ce qui entraîne des variations éventuellement non-linéaires de la structure de réseau.

Abstract. The results of our infrared reflectance studies of single and mixed alkali borate glasses are reviewed and discussed in the context of the network structure and the interactions between alkali cations and their sites in the glass. In particular, we focus on the strong influence of the alkali cation type, content, and alkali substitution on the structure of the network building units. The dominant role of alkali ions also emerges from the analysis of their motion bands active in the far-infrared. Thus, the presence of two different distributions of anionic site environments was found to characterise the single alkali borate glasses. The corresponding analysis of the mixed alkali glass spectra revealed the existence of interactions between the dissimilar alkalis, which strongly affect their bonding characteristics. The new bonding requirements drive the glass network to perform suitable rearrangements, leading eventually to non-linear variations of the network structure with alkali substitution.

1. INTRODUCTION

Glasses with high ionic conductivities have attracted wide interest because their advantages over corresponding crystalline conductors make them suitable for electrochemical applications. The continuing search for better glassy conductors has led to the discovery of many new compositions (1-3), with some Ag^+ and Cu^+ ion conducting glasses exhibiting room temperature conductivity greater than 0.1 S cm^{-1} (4). However, despite the great number of studies devoted to ionically conducting glasses the mechanism of ion transport remains poorly understood. This is particularly evident from the fact that no theory on ionic conduction in glasses has yet received general acceptance. In this context, the need for a better understanding of glass structure is recognized, with emphasis placed upon those structural aspects which are related to ionic mobilities (5).

Among the various spectroscopic techniques currently available, the potential of infrared spectroscopy for investigations of glass structure has been well documented (6). In addition, modern Fourier-transform infrared spectrometers working in the reflectance mode provide the ability for data acquisition over a broad and continuous spectral range, without the need of changing sample

form or thickness, a problem usually encountered in transmission measurements. This advantage, combined with the fact that proper data analysis yields absolute values of the optical and dielectric properties of glass, make the infrared reflectance technique an important tool in glass science. In this paper we review some aspects of our recent infrared reflectance investigations on alkali borate glasses. In particular, we first present results on the single alkali diborate glasses, $M_2O \cdot 2B_2O_3$ ($M=Li, Na, K, Rb, Cs$), with the purpose of demonstrating the predominant role of alkali ions on the structures assumed by the boron-oxygen network. Structural variations are conveniently probed in the mid-infrared ($ca\ 400-1600\ cm^{-1}$) where the vibrations of the borate skeleton are mainly active. The interactions between the alkali ions and their anionic sites are also investigated through the alkali motion bands in the far-infrared (below $ca\ 500\ cm^{-1}$). Studies of this kind shed light on the nature of sites available for the alkalis and thus on the way these cations are distributed in the glass. The relevance of such information to ion transport properties is quite obvious.

The second part of this paper involves the evolution of the network structure as the alkali oxide content is progressively changed. The ability to form glasses in a large and continuous range (up to 73 mol % Li_2O) makes the $xLi_2O \cdot (1-x)B_2O_3$ system ideal for this purpose. The study of the mid-infrared spectra was undertaken to reveal the structure of the boron-oxygen arrangements constituting the borate network and their dependence on the Li_2O content. Since the various borate groupings also constitute the anionic sites hosting the Li^+ ions, their effect on the lithium rattling motions was investigated.

One special problem related to ionic transport in glasses is the well known mixed alkali effect (MAE), which is mainly associated with the large non-linear decrease in ionic conductivity upon replacement of one alkali ion by another. Despite the universality of the MAE and the large number of theories proposed for its explanation, its origin remains highly controversial (7-9). Studies of the structure of mixed alkali glasses are most desirable, considering the complicated behavior of these ionic systems. The third part of this work deals with mixed alkali diborate glasses, $xM_2O \cdot (1-x)M'_2O \cdot 2B_2O_3$, with the purpose of investigating the existence of structural peculiarities that could be related to the MAE.

Borate glasses have been chosen as "prototypes" in our research on ionic glasses, even though the phenomena investigated are quite general. This choice is based mainly on the richness of the borate chemistry, that enables the spectroscopic probing of even subtle structural changes, which could remain at first unnoticed in other glass forming systems. Nevertheless, extension of our studies to various other systems is in progress to test the generality of trends observed in borate glasses.

2. EXPERIMENTAL PROCEDURES

Glasses were prepared from the stoichiometric amounts of metal carbonates and B_2O_3 . The thoroughly mixed batches were melted in platinum crucibles at $900-1200^\circ C$ for 10-30 min and subsequently quenched between two preheated and polished copper blocks. Glass samples with good surfaces were obtained and used for spectroscopic measurements without further treatment.

Infrared reflectance studies were performed on a Fourier-transform vacuum spectrometer (Bruker 113v), equipped with the appropriate reflectance attachment, sources, detectors and beam splitters for an effective coverage of the $30-4000\ cm^{-1}$ frequency range. Each spectrum represents the average of 200 scans measured at room temperature with $2\ cm^{-1}$ resolution.

The reflectance data were analysed by the Kramers-Kronig transformation method to obtain the frequency dependent phase angle between reflected and incident wave. The reflectivity and phase angle spectra were subsequently employed to calculate the optical and dielectric properties (10). Infrared data reported in this work are in the form of absorption coefficient spectra.

3. RESULTS AND DISCUSSION

3.1. The Influence of Alkali Cations on the Network Structure and Their Localized Vibrations

The infrared absorption spectra of alkali diborate glasses are shown in Fig. 1, where they have been upshifted to facilitate comparison. It is clear that the overall spectral profiles and the absolute values of the absorption coefficient depend strongly on the type of the modifier cation. To understand the origin of the observed differences it is instructive to briefly review the spectral assignments proposed for the various absorption features (10-13). The mid-infrared spectra are dominat-

Fig. 1. Infrared absorption spectra of alkali diborate glasses, $M_2O \cdot 2B_2O_3$ (11,12).

Fig. 2. Normalized infrared area, A_4 , of the spectral region between 800 and 1180 cm^{-1} , versus the fraction of four-coordinated boron atoms, N_4 (11,12).

ed by three complex absorption profiles which can be attributed to vibrational modes of the borate network: $550\text{--}800\text{ cm}^{-1}$ (deformation modes of the network), $800\text{--}1200\text{ cm}^{-1}$ (B-O asymmetric stretching modes of BO_4 tetrahedra) and $1200\text{--}1550\text{ cm}^{-1}$ (B-O asymmetric stretching modes of BO_3 triangles).

Of particular interest is the part of the spectrum originating from the absorption of network segments containing BO_4 tetrahedra. The asymmetric absorption profile ($800\text{--}1200\text{ cm}^{-1}$) suggests the presence of boron tetrahedra in various borate groupings (10), while its obvious dependence on the type of alkali is indicative of the influence of the latter on the glass structure. To quantify this effect we have evaluated the integrated absorption in the $800\text{--}1200\text{ cm}^{-1}$ frequency range and normalized it by multiplying with the corresponding glass molar volume to account for differences in density (12). The so-obtained normalized absorption due to BO_4 tetrahedra, A_4 , is plotted in Fig. 2 against the fraction of four-coordinated boron atoms, N_4 . This is a parameter frequently employed to discuss the structure of borate glasses, and is usually obtained from the analysis of NMR spectra (14). The two sets of independent data are related linearly, showing the influence of alkali ion on the network structure: the fraction of four-coordinated boron atoms decreases upon increasing alkali size. Since the alkali content is constant it is expected that the fraction of boron triangles containing non-bridging oxygens should increase from Li to Cs. This trend was found to be supported by the results of a comparative Raman study of alkali borate glasses having a fixed alkali content (15).

The above results contradict the early belief that the borate structure is solely a function of the alkali content, and is independent of the nature of alkali ion. The direct influence of alkalis on the glass structure is another manifestation of the important role played by the modifier cations in the glass forming process. It has been suggested that the need to build up the appropriate coordination

Fig. 3. Deconvolution of the far-infrared spectra of $M_2O \cdot 2B_2O_3$ glass (continuous lines) into Gaussian component bands (dashed lines) (12).

environment for the modifier cations is one of the driving forces that dictate the nature of structures assumed by the glass network (16,17). The establishment of characteristic coordinations of metal ions in glasses has been shown by EXAFS (18, 19) and more recently by neutron scattering experiments (20). It is therefore of prime interest to study the far-infrared region where absorptions due to vibrations of metal ions in their equilibrium sites in glass are measured (10-13).

Figure 3 shows that the far-infrared profiles of the alkali diborates are characterized by pronounced asymmetries, suggesting the existence of more than one band. Deconvolution of these spectra resulted in the Gaussian component bands also shown in the same figure (12). It was argued that the high frequency component of Li (579 cm^{-1}) and those of Rb (187 cm^{-1}) and Cs (160 cm^{-1}) glass spectra can be attributed to deformation and libration modes of network segments, respectively (12). The remaining two bands at lower frequencies for Li, Rb and Cs and those of Na and K are considered further for investigation. Figure 4 depicts the frequencies of these bands designated by ν_H and ν_L (H for the high- and L for the low-frequency band respectively) versus the inverse square root of cation mass, $m_c^{-1/2}$. The linear relation shown in this figure strongly suggests that both bands originate from vibrations of alkali cations in their suitable anionic environments, in agreement with earlier transmission studies (21).

It was argued elsewhere (22) that the presence of two cation-motion bands cannot be accounted for by symmetry reduction effects alone and/or coordination geometry variations and isotope effects. It is realized that such effects are certainly present in glasses, but their magnitude is not sufficient to cause the appearance of two bands. Their effect is to simply contribute to the broadening of each individual band. Instead, we have suggested that the two far-infrared bands denote the existence of two different distributions of anionic site environments (10-13, 21, 22). This is also supported by the plots in Figure 5(a), where the relative bandwidths $\Delta\nu/\nu$ are shown ($\Delta\nu$ is the full width at half maximum and $\nu = \nu_H, \nu_L$). Two different families are formed and characterize the low-(L) and high-(H) frequency bands, with the relative bandwidth of the former being more than twice than that of the latter bands. The relative area of the L bands is also shown in Figure 5(b). Clearly, the cation-motion activity is distributed approximately equally over L and H sites for Li, but this picture chang-

Fig.4. Cation-motion frequencies versus $m_c^{-1/2}$.

Fig.5. Alkali dependence of the relative bandwidths $\Delta\nu/\nu$ (a) and of the relative area of the low-frequency component band $A_L/(A_H + A_L)$ (b) (12).

es gradually in favour of the H sites upon increasing alkali ion size.

A key difference between cations giving rise to the H bands and those responsible for the L bands concerns their effective charge. Calculations based on cation-motion frequencies (10), as well as on the transverse optical-longitudinal optical splitting (12) have shown that cations residing in L sites have a lower effective charge than those in H sites. Charge neutrality considerations suggest that the same trend should apply for the negative charge of the corresponding anionic sites.

The question that emerges now concerns the origin of the two distributions of anionic sites. The early SAXS work of Porai-Koshits and coworkers has ruled out phase separation in alkali borate glasses (23). Instead, their results were interpreted in terms of structural inhomogeneities (about 15 Å in size) called "pseudophases". Other structural models also support the "granularity" of glass structure and propose the presence of relatively ordered material ("clusters") connected by highly disordered regions ("connective tissue") (24-27). Recent computer simulation studies of alkali silicate glasses by Huang and Cormack have shown that a nanoscale inhomogeneity is inherent to these glasses (28,29). This is manifested by an inhomogeneous distribution of alkali ions which leads to alkali rich and silica rich regions. If such an inhomogeneous glass structure also holds for borate glasses, then cations present in the alkali rich regions should vibrate at higher frequencies (H band) than those situated in the alkali poor regions (L band) (30). In this context, our far-infrared results are compatible with an inhomogeneous borate glass structure. Further information concerning the borate structural elements that could be responsible for such phenomena are presented in the next section.

3.2. Dependence of Network Structure and Anionic Site Distributions on Alkali Content

Infrared absorption spectra of $x\text{Li}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$ glasses spanning the entire glass forming region are shown in Fig. 6. It is evident that increasing the amount of Li_2O causes drastic spectral variations, which of course manifest corresponding changes of the network structure. For example,

Fig. 6. Infrared spectra of $x\text{Li}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$ glasses (10).

the absorption envelope characterizing BO_4 tetrahedra ($800\text{--}1200\text{ cm}^{-1}$) gains relative intensity upon increasing x , reaches its maximum at $ca\ x=0.4$ and then it decreases upon further addition of Li_2O . Therefore, the initial creation of BO_4 -containing groups and their subsequent destruction in favour of units containing non-bridging oxygens is inferred. Typical units of the latter type are the chain-type metaborates $(\text{B}\text{O}_2\text{O}^-)_n$ (O =bridging oxygen atom) with characteristic absorption at 1240 cm^{-1} , the pyroborates $\text{B}_2\text{O}_3^{4-}$ (1130 cm^{-1}) and the highly charged orthoborate triangles (1300 cm^{-1}) formed at very high lithium contents.

A detailed deconvolution of the infrared spectra (10) has led to the evaluation of the normalized band area of each characteristic borate unit as a function of Li_2O content (Fig.7). The symbol BO_4^- in this figure indicates a wide diversity of borate units containing BO_4 tetrahedra, such as the pentaborates, triborates, diborates, "loose" and γ -type BO_4 tetrahedra (10,31). Figure 7 illustrates a spread in the nature of the borate units present at each Li_2O content. Thus, borate arrangements with modification levels (i.e. negative charge per boron center) below that dictated by stoichiometry, as well as equal and above that, are coexisting. A direct consequence of such a diversity of network-building units would be that the local concentration of the chargebalancing Li^+ cations is not uniform throughout the glass structure. Lithium cations present in glass regions of lower degree of modification would experience a lower anionic charge and thus vibrate at lower frequencies than those present in higher modified regions (30). The former cations would contribute to the L band and the latter to the H band observed in the far-infrared.

What is of interest here is the fact that, despite the large variations of the network structure with alkali content observed here and elsewhere (15,32), the far-infrared spectra can always be simulated well by two broad alkali motion bands (10,21). We have observed that the same two band be-

Fig. 7. Normalized infrared band areas of borate units found in lithium borate glasses (10).

havior characterizes the far-infrared spectra of alkali-silicate, molybdate and other glass forming systems (work in progress). These results support the conclusion that the existence of *two distinct distributions of anionic site environments*, arising from an inhomogeneous distribution of metal cations, should be intrinsic to such binary glasses.

3.3. Structural Aspects of Mixed Alkali Glasses.

In the previous sections we gave examples of the network structure and the localized alkali vibrations in binary borate glasses. We turn now our attention to the more complicated mixed alkali glasses with the purpose of learning more about their behavior. Typical infrared spectra are shown

Fig. 8. Infrared spectra of mixed alkali borate glasses $x\text{Li}_2\text{O} \cdot (1-x)\text{Cs}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ (11).

Fig. 9. The normalized infrared area of the $800\text{--}1180 \text{ cm}^{-1}$ region of $x\text{M}_2\text{O} \cdot (1-x)\text{Cs}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glasses (11).

in Figure 8 for glasses in the Li-Cs mixed diborate system. It can be seen that a progressive replacement of one alkali by another results in systematic variations of the infrared response. It is of interest to examine whether these spectral variations with x could result from a linear change of glass structure with alkali substitution.

Following the discussion of Section 3.1, the normalized infrared areas in the range 800-1180 cm^{-1} were obtained in order to probe the dependence of the concentration of BO_4 tetrahedra on the substitution parameter x . The results are shown in Figure 9, where data for the other three M-Cs diborate systems ($M=\text{Na}, \text{K}, \text{Rb}$) are given for comparison. A very interesting non-linear variation of A_4 with x has emerged, suggesting that the network structure of mixed alkali glasses cannot be described by a linear combination of the structures of the end member glasses ($x=0,1$). For the particular case investigated this effect is well pronounced in the Li-Cs and Na-Cs systems, but tends to disappear as the difference between the dissimilar alkalis becomes smaller. A similar reduction of N_4 from additivity was observed by Zhong and Bray for diborate glasses of maximum mixing, $x=0.5$ (14). Since the total alkali content in the system is constant, the trends in Fig.9 suggest that the fraction of non-bridging oxygens should exhibit a positive departure from linearity upon alkali mixing.

Consideration of the far-infrared parts of the spectra in Fig.8 shows immediately that the intensity of the Cs^+ motion band decreases upon increasing x as expected, and that this is also accompanied by a parallel decrease in its peak frequency. This frequency variation with x is an important result, that contradicts earlier findings that the cation motion frequency in mixed alkali glasses is independent of x (17, 33-36). The new results suggest that the Cs-oxygen interactions are affected by Li^+ cations and become weaker than those in the binary glass ($x=0$). However, conclusions about the corresponding Li-oxygen interactions cannot be drawn on the basis of the far-infrared profiles alone, because of the large bandwidth of the Li^+ motion band (at ca 400 cm^{-1}). This difficulty calls for a systematic deconvolution of the far-infrared spectra of mixed alkali glasses.

An example of such an analysis is shown in Figure 10 for compositions in the Na-Cs diborate system (13). It was found that a mathematically adequate and chemically meaningful simulation of the mixed alkali glass spectra requires at least four component bands. The two lower frequency ones (at ca 50 and 100 cm^{-1}) were assigned to Cs^+ motions and those at higher frequencies (ca 150-160 and 240 cm^{-1}) to Na^+ motions in mixed alkali glasses. It can be seen that the frequencies of Cs^+

Fig. 10. Deconvoluted far-infrared spectra of $x\text{Na}_2\text{O} \cdot (1-x)\text{Cs}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glasses (13).

Fig.11 Cs^+ motion frequencies in $x\text{M}_2\text{O} \cdot (1-x)\text{Cs}_2\text{O} \cdot 2\text{B}_2\text{O}_3$ glasses (11).

shift to lower values with decreasing the amount of Cs in the glass. To the contrary the Na^+ motion frequencies show an upshift with decreasing the Na content. It is thus evident that the alkali - oxygen interactions are affected by alkali mixing. Specifically, the metal-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 in the mixed alkali glass.

The interactions between the dissimilar alkalis were found to depend on their field strength difference as shown in Figure 11, where the Cs^+ motion frequencies are used as convenient probes of such interactions. It is seen that the larger the difference between the alkali partners the larger the decrease of the ν_{H} frequency of Cs^+ . The frequency of the low component band, ν_{L} , show a smaller dependence on either M or x.

The results of this section suggest that attempts to resolve the mystery of the mixed alkali effect should consider the clear influence of one alkali on the other. The presence of interactions between dissimilar alkalis manifests their close proximity in network-mediated "pair" configurations (16,37). Once the two unlike alkalis are brought to each others vicinity the difference in their polarizing power leads to alterations of the individual bonding/ coordination conditions (38,39), as compared to the ones assumed by the alkalis in the binary systems. The new "pair" configuration is presumably more stable and thus it effectively reduces the ionic mobilities. The glass network responds to fulfil the new bonding requirements, imposed by the alkalis, by performing suitable rearrangements that may result in non-linear structural variations. It appears that in the case of borate glasses such a rearranging process involves the transformation of BO_4 tetrahedra into their isomeric borate triangles with non-bridging oxygen, which render the network a higher flexibility to meet the new bonding conditions.

4. CONCLUSIONS

The infrared reflectance study of single and mixed alkali borate glasses has led to a number of interesting points regarding these typical ionic systems. First, the structure of the borate network was found to depend strongly on the alkali content, as well as on the type of alkali employed. Alkali substitution in mixed alkali glasses was shown to lead to non-linear variation of the network structure. Second, the analysis of the far-infrared absorption profiles of single alkali glasses showed the presence of two distributions of anionic sites regardless of the details of the network structure. This fact was associated with an inhomogeneous distribution of alkali ions, in agreement with the wide diversity of the network-building borate groups. Third, the frequencies of the alkali motion bands in mixed alkali glasses were found to vary with alkali substitution, suggesting the presence of dissimilar alkalis in "pair" configurations, and the existence of strong interactions that affect the ionic mobilities. Investigations on other glass forming systems are in progress to examine the possible generality of the effects reported here.

Acknowledgement

The author gratefully acknowledges the many stimulating discussions with Dr. G.Chryssikos and the careful experimental work of A. Patsis and J. Kapoutsis reviewed here. This work was supported by NHRF.

REFERENCES

1. A. Schiraldi, *Electrochim. Acta* 23 (1978) 1039.
2. E. Robinel, B.Carette and M.Ribes, *J. Non-Cryst. Solids* 57 (1983) 49.
3. T. Minami, *J. Non-Cryst. Solids*, 73 (1985) 273.
4. N. Machida, Y. Shinkuma and T. Minami, *J. Ceram. Soc. Jpn.* 97 (1989) 1104.
5. M. D. Ingram, *Philos. Mag. B* 60 (1989) 729.
6. J. Wong and C. A. Angell, 1976, in *Glass Structure by Spectroscopy* (New York, Dekker).
7. J. O. Isard, *J. Non-Cryst. Solids* 1 (1969) 235.
8. D. E. Day, *J. Non-Cryst. Solids*, 21 (1976) 343.
9. M. D. Ingram, *Phys. Chem. Glasses*, 28 (1987) 215.
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, *Proceedings of VII International Conference on the Physics of Non-Crystalline Solids*, Cambridge, 1991 (to be published by Taylor and Francis).

12. E. I. Kamitsos, A. P. Patsis and G.D.Chryssikos, J. Non-Cryst. Solids, submitted (1991).
13. E. I. Kamitsos, A. P. Patsis and G.D. Chryssikos, Phys. Chem. Glasses, 32 (1991) 219.
14. J. Zhong and P.J.Bray, J. Non- Cryst. Solids, 111 (1989) 67.
15. G.D.Chryssikos, E.I.Kamitsos and M. A. Karakassides, Phys. Chem. Glasses 31 (1990) 109.
16. A. H. Dietzel, Phys. Chem. Glasses, 24 (1983) 172.
17. E. I. Kamitsos and W. M. Risen, J. Non-Cryst. Solids, 65 (1984) 333.
18. G. N. Greaves, J. Non-Cryst. Solids, 71 (1985) 203.
19. G. N. Greaves, Philos. Mag. B60 (1989) 793.
20. P. H. Gaskell, M. C. Barnes and P. Chieux, Nature 350 (1991) 675.
21. E. I. Kamitsos, M. A. Karakassides and G.D.Chryssikos, J. Phys. Chem. 91 (1987) 5807.
22. E.I.Kamitsos, G.D. Chryssikos, A. P. Patsis and M.A.Karakassides, J. Non-Cryst. Solids 131-133 (1991) 1092.
23. E. A. Porai- Koshits, J. Non-Cryst. Solids , 73 (1985) 79, and references therein.
24. C.H.L.Goodman, Phys. Chem. Glasses 26 (1985) 1.
25. T.Minami, K. Imazawa and M.Tanaka, J. Non-Cryst. Solids 42 (1980) 469.
26. K. J. Rao and C.N.R. Rao, Mater. Res. Bull. 17 (1982) 1337.
27. M.D. Ingram, M. A. Mackenzie, W. Müller and M.Torge, Solid State Ionics 28 (1988) 677.
28. C. Huang and A.N. Cormack, J. Chem. Phys. 93 (1990) 8180.
29. C. Huang and A.N. Cormack, J. Chem. Phys. 95 (1991) 3634.
30. E.I.Kamitsos, J. Phys. Chem. 93 (1989) 1604.
31. G.D.Chryssikos, E. I. Kamitsos, A. P. Patsis, M.S. Bitsis and M. A. Karakassides, J. Non-Cryst. Solids 126 (1990) 42
32. E.I.Kamitsos and M.A. Karakassides, Phys. Chem. Glasses 30 (1989) 19
33. G.B. Rouse, P.J.Miller and W.M. Risen, J. Non-Cryst. Solids 28 (1978) 193
34. G. D. Minser and W.B. White, 1984 in Spectroscopic Investigations of Glass Structure, U.S.Department of Energy Annual Report no DOE/ ER / 450077-1.
35. N. Soga and K.Hirao, 1986, in Structure and Bonding in Non Crystalline Solids. Edited by G.E. Walrafen and A. G. Revesz (New York, Plenum)
36. A. Doi, Phys. Chem. Glasses 30 (1989) 83.
37. O.V.Mazurin, 1965, in The Structure of Glass (New York, Consultants Bureau) vol. IV, p.5
38. J. Lumsden, Discussions Faraday Soc. 32 (1961) 138
39. C.T. Moynihan and R.W.Laity, J. Phys. Chem. 68 (1964) 3312.