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USE OF LASERS IN THE STUDY OF THE GLASSY STATE

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ABSTRACT

Laser Raman spectroscopy has been employed over the years to study the structure of a variety of glass systems, with the purpose of understanding a number of phenomena encountered in them, such as the "borate anomaly", the "mixed network" and the "mixed alkali" effects. In this paper we review the results of Raman spectroscopic investigations of some characteristic borate glasses: B_2O_3 , the sodium-borate as well as the Li and Cs-borate glasses of the same alkali content. The results are compared with those of other techniques and used to provide a structural basis for the composition dependence of a number of glass physical properties.

INTRODUCTION

The structure of glasses has long been the subject of much controversy due to their unique characteristics (glasses possess many of the mechanical properties of crystalline solids and yet they lack the long-range order of crystalline materials). Thus, many of the most sensitive structural probes including diffraction techniques, are unable to reveal detailed structural information about glasses.

During the last two decades, following the discovery of lasers, Raman spectroscopy has become a powerful technique for the investigation of the glass structure [1-3]. In this paper we review some representative examples of laser Raman spectroscopic studies of borate glasses, including glassy B_2O_3 and sodium borates of a wide composition range. It is shown that Raman spectroscopy is very useful in probing the continuous structural variations of the borate network, induced by addition of Na_2O to B_2O_3 . The information obtained from the Raman spectra is important in understanding the structural basis for the non-linear composi-

tional variation of many physical properties, known as the "borate anomaly" effect. Also, Raman spectra of Li and Cs - borate glasses are presented and discussed. They demonstrate that the nature of the alkali action plays a crucial role in determining the structure of the glass network, contrary to previous belief.

GLASS STRUCTURE BY LASER RAMAN SPECTROSCOPY

THE STRUCTURE OF GLASSY B_2O_3

Vitreous B_2O_3 has been one of the most studied materials over the years. A variety of models proposed for its structure have been reviewed in a number of articles [4,5]. The originally accepted ideas for the structure of glassy B_2O_3 have been based on a random network of corner-linked BO_3 triangles, as first suggested by Zachariasen [6].

Later on, Goubeau and Keller [7] proposed that glassy B_2O_3 consists primarily of planar six-membered boroxol rings ($B_3O_{4.5}$), which are randomly interconnected by bridging oxygens or other smaller units. Their proposition was based on the presence of an extremely sharp peak at 806 cm^{-1} in the Raman spectrum of glassy B_2O_3 . The spectrum is shown in figure 1 and was taken from the work of Galeener et al. [8]. The polarized (HH and HV) Raman spectra are depicted, with HH and HV indicating that the incident and scattered electric vectors are parallel and perpendicular respectively. Quite unusually for a glass spectrum, the 806 cm^{-1} band has full width at half-maximum of 15 cm^{-1} only, while it also exhibits a high degree of polarization: $HH/HV \approx 28$. It is interesting to note that a similar feature is absent from the infrared spectrum of glassy B_2O_3 .

It is apparent that the Raman-active 806 cm^{-1} band should be due to a totally symmetric vibration of an appropriate structural unit, i.e., a unit which can allow for such a vibration to occur. Along these lines, Coubeau and Keller [7] assigned the 806 cm^{-1} band to the symmetric ring breathing vibration of the boroxol ring, involving mainly the oxygen atoms in the ring (Fig.2a). It is worth noting that crystalline B_2O_3 , which is known to consist of a three-dimensional network of interlinked BO_3 triangles, exhibits no Raman band in the frequency region around 800 cm^{-1} [9].

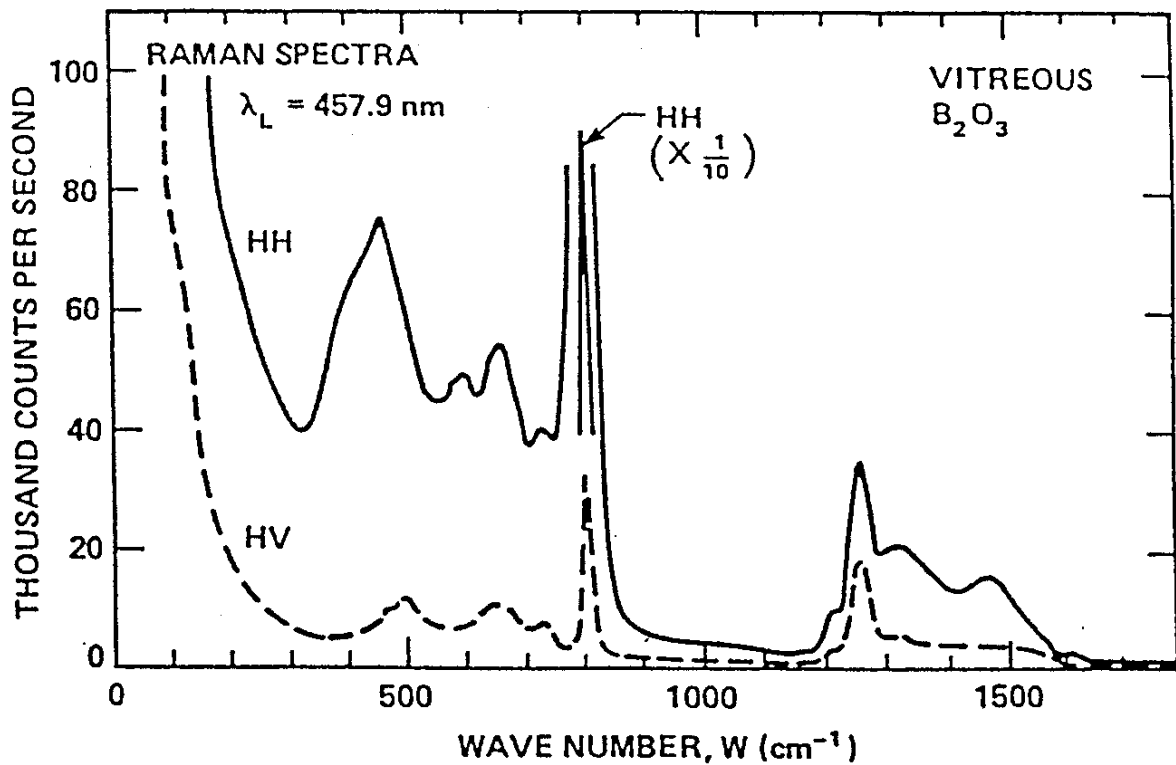


Fig. 1. Polarised Raman spectra of glassy B_2O_3 (8).

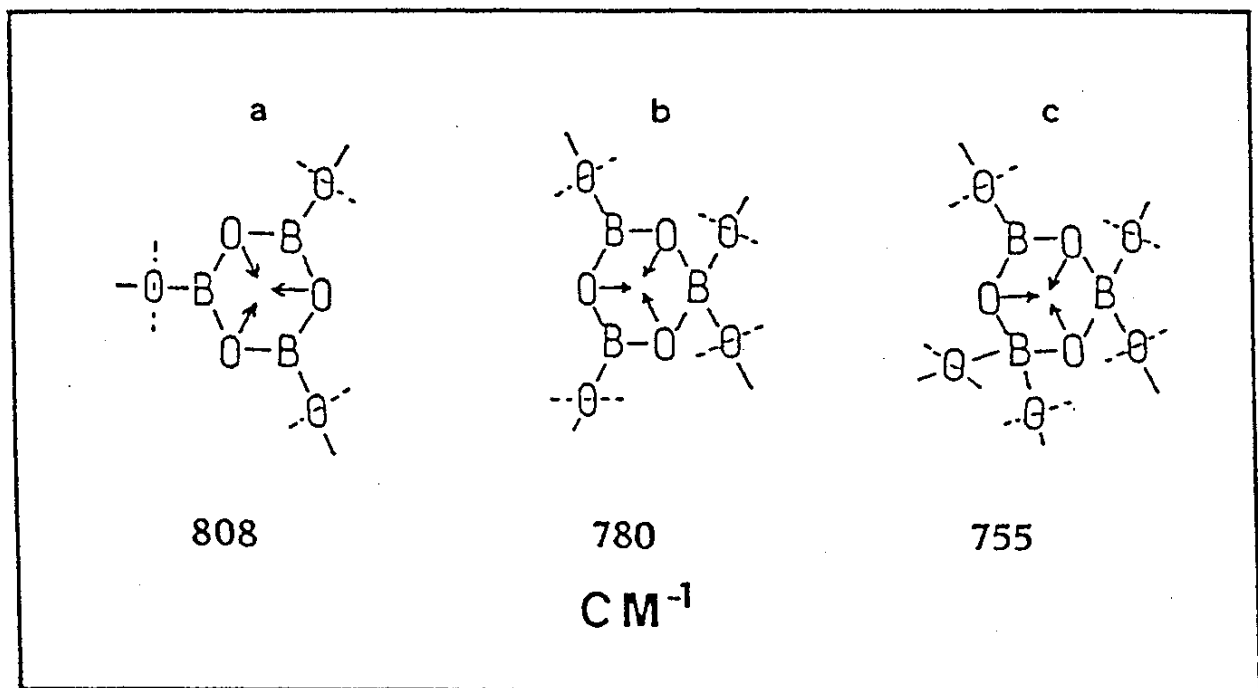


Fig. 2. Frequencies and eigenvectors of the ring breathing vibration of boroxol ring (a), six-membered ring with one BO_4 tetrahedron (b), and six-membered ring with two BO_4 tetrahedra (c) [12, 23].

Krogh-Moe [10] and Kristiansen and Krogh-Moe [11] performed a vibrational analysis on the boroxol ring, and found that the 806 cm^{-1} frequency is insensitive to changes in the atoms bound to the ring, in

agreement with the assignment proposed by Goubeau and Keller. Thus, it is the completely localized nature of this vibration, i.e., its decoupling from the rest of the borate network, which is responsible for the exceptionally small bandwidth of the 806 cm^{-1} band.

Further spectroscopic support for the existence of boroxol rings in glassy B_2O_3 , as well as, for the origin of the 806 cm^{-1} Raman band, has been provided by the study of oxygen- and boron- isotopically substituted B_2O_3 glasses reported by Windisch and Risen [12]. Figure 3 depicts the Raman spectra (800 cm^{-1} region) of B_2O_3 glasses, for different types and amounts of isotopic substitution. Figure 3a shows that complete substitution of ^{16}O by ^{18}O causes a downshift of the ring-breathing frequency by 48 cm^{-1} , without any detectable broadening. When 50% of ^{16}O is replaced by ^{18}O , ($^{11}\text{B}_4\text{ }^{16}\text{O}_3\text{ }^{18}\text{O}_3$ glass), then the 806 cm^{-1} band of the $^{11}\text{B}_2\text{ }^{16}\text{O}_3$ glass (Fig. 3a) is replaced by a set of four bands at 808, 791, 777 and 760 cm^{-1} , having the intensity relationship 1:3:3:1 (Fig. 3b). On the contrary, complete (Fig. 3c) or partial (Fig. 3d) substitution of ^{11}B by ^{10}B causes neither shift nor broadening of the 808 cm^{-1} band. This clearly demonstrates the fact that the vibrational mode responsible for this band involves motion of the ring oxygen atoms only.

While the above results are consistent with the ring breathing vibration of boroxol rings, the behavior of other Raman bands upon isotopic substitution is quite different. Of interest is the 1260 cm^{-1} band, which was found to exhibit a network-type behavior; it shifts without broadening upon both oxygen- and boron-isotopic substitution. Thus, it was concluded that Raman isotopic data indicate a B_2O_3 - glass structure consisting of both boroxol rings and a continuous random network of connecting bonds [12].

In relation to the above we note that the X-ray correlation function for glassy B_2O_3 derived by Mozzi and Warren [13], is consistent with a network composed mainly of boroxol rings. In addition, the NMR studies of Bray and coworkers [14, 15] suggest that the majority of boron atoms are in boroxol rings, the remaining being in planar BO_3 triangular units. In agreement with these studies, recent neutron diffraction investigations of glassy B_2O_3 indicate a mixed boroxol ring- independent BO_3 triangle network, with about 60% of boron atoms participating in boro-

xol rings [5,16]. Contrary to these results, earlier [17] and recent [18] molecular dynamic (MD) simulations of B_2O_3 have failed to predict the presence of boroxol rings, and instead, they yield a network of corner-linked BO_3 triangles. It has been argued, however, that this originates from the fact that such MD studies using purely ionic potentials, neglect covalent boron- oxygen interactions [19,20]. Moreover, the additional stabilization energy of the "aromatic" boroxol rings was completely omitted [20].

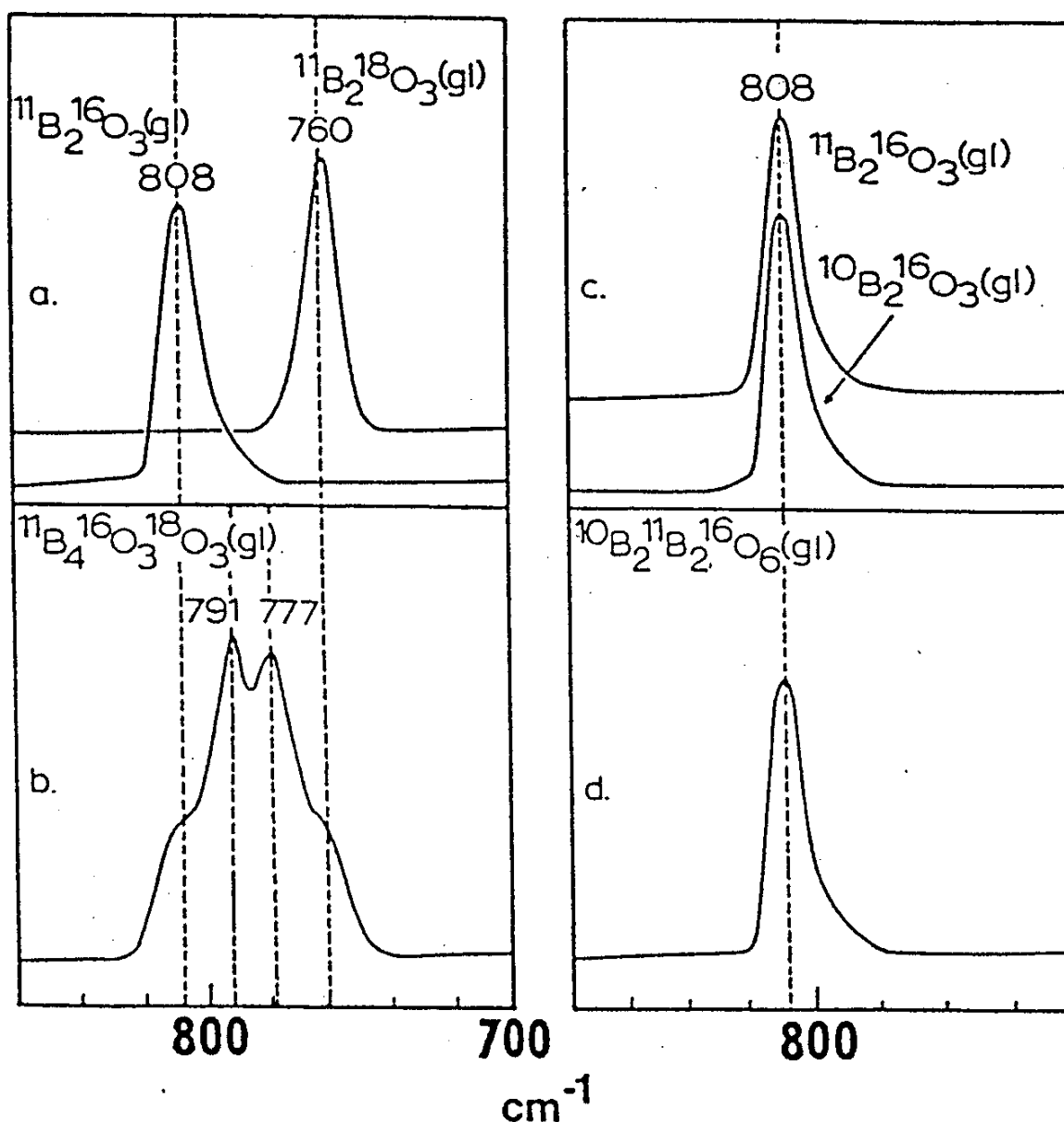


Fig. 3. Raman spectra of B_2O_3 glasses for different types and amounts of boron- and oxygen isotopic substitution [12]

It was demonstrated in this section that Raman spectroscopy, in agreement with other techniques, provides evidence for the presence of boroxol rings in the structure of B_2O_3 glass.

THE STRUCTURE OF BINARY SODIUM- BORATE GLASSES

Boron trioxide glass is a very good glass forming oxides and provides the basis for a great variety of borate- glass systems. Addition of alkali metal oxides (M_2O) to B_2O_3 results in a class of borate glasses, having a general formula $x M_2O \cdot (1 - X) B_2O_3$. Such glass systems are of special interest for two main reasons: First, some of them are good ionic conductors, or can be used to prepare more complicated fast ionic conducting glasses, and second, most of their physical properties show a pronounced non - linear dependence on M_2O content, x , [21]. The latter phenomenon termed as the "borate anomaly" effect, while known for some time, still lacks an adequate structural interpretation. This fact, combined with the technological importance of these materials, demands a good knowledge of their structural characteristics.

In this section we present and discuss the Raman spectra of sodium-borate glasses: $x Na_2O \cdot (1-x) B_2O_3$, which have been prepared in an extended glass forming region: $0 \leq x \leq 0.75$. The Raman spectra of low modification glasses are shown in figure 4, for several values of x . The most important effect of increasing the Na_2O content is the rapid decrease of the intensity of the 806 cm^{-1} peak, with the simultaneous development of a band at ca. 770 cm^{-1} . For the glass composition $x=0.25$ the 806 cm^{-1} band has disappeared, indicating the absence of boroxol rings, while the 765 cm^{-1} band becomes the dominant Raman feature.

The latter feature was assigned by Brill [23] and Windisch [24] to the symmetric ring - breathing vibration of six - member rings containing one or two BO_4 tetrahedra (Fig. 2b, c). Rings of this kind are incorporated into larger borate arrangements, such as the tetraborate, pentaborate or the dipentaborate groups [25]. Thus, the Raman spectra of figure 4 indicate that addition of Na_2O to B_2O_3 causes the progressive transformation of boroxol rings into rings with BO_4 tetrahedra, i.e., a change of boron coordination number from three to four. These results are in agreement with the NMR studies of Bray [26], which have demonstrated that an increase of the fraction of four- coordinated boron atoms, N_4 , occurs upon increasing x .

Addition of Na_2O to B_2O_3 at even higher contents causes drastic spectral effects, as shown in Figure 5 for the $0.35 \leq x \leq 0.55$ Na - borate glasses [27]. These Raman spectra exhibit a large number of bands,

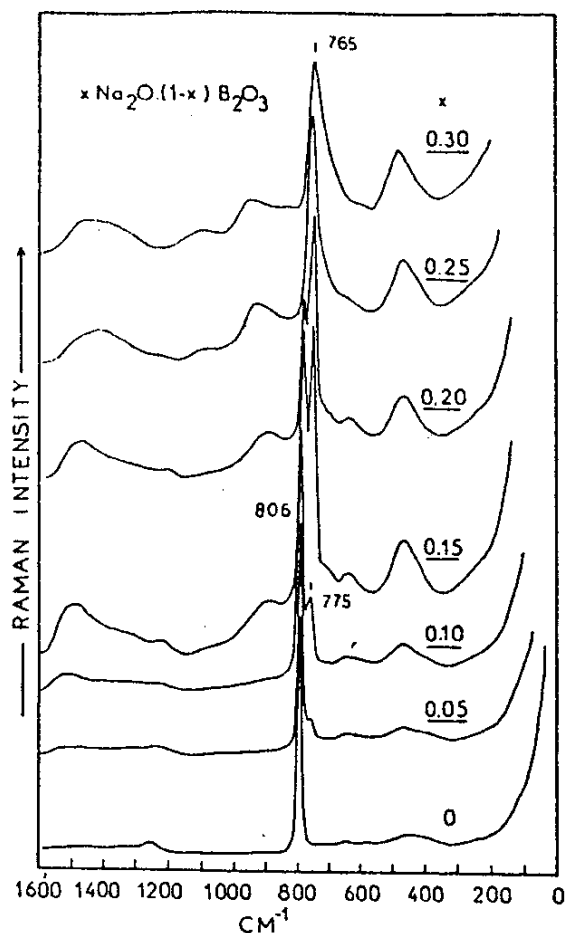


Fig. 4. Raman spectra of $x \text{Na}_2\text{O} \cdot (1-x) \text{B}_2\text{O}_3$ glasses in the composition range: $0 \leq x \leq 0.30$ [22].

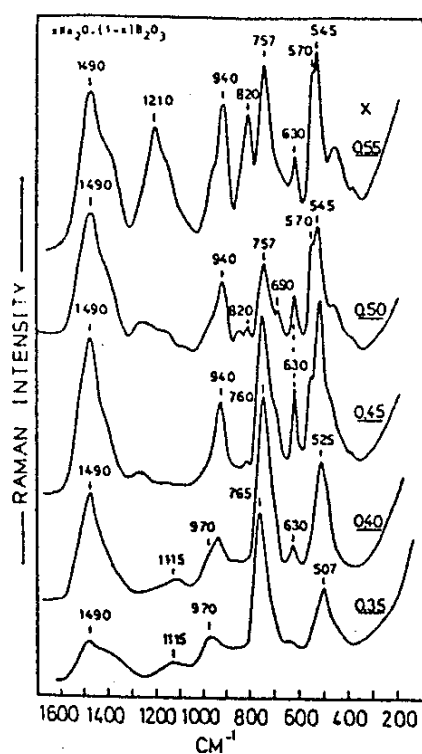


Fig. 5. Raman spectra of $x \text{Na}_2\text{O} \cdot (1-x) \text{B}_2\text{O}_3$ glasses in the composition range $0.35 \leq x \leq 0.55$ [27]

however, the compositional dependence of a few of them will be discussed here. A more detailed discussion can be found elsewhere [27]. Of particular interest is the band at 630 cm^{-1} , which appears first at $x=0.35$ and develops with x . The presence of this band indicates the formation of ring-type metaborate units (Fig. 6a), since it originates from the ring breathing vibration of such units [23]. A new band at 820 cm^{-1} appears in the Raman spectrum of the $x=0.45$ glass and becomes a dominant feature upon further increasing x . This band, as well as, the one at 1210 cm^{-1} , are characteristic of the presence of pyroborate ($\text{B}_2\text{O}_5^{4-}$) units (Fig. 6b). They originate from the symmetric stretching vibration of B - O - B bridges and terminal B - O⁻ bonds respectively [27]. Thus, the sequence of the Raman spectra in figure 5 demonstrates that addition on Na_2O in this composition range, causes the progressive disruption, i.e., deployment of the borate network through formation of non-bridging-oxygen-containing borate units. Such representative units are the metaborate rings and the pyroborates, both being of "molecular" type, i.e., completely dismantled from the covalently connected borate network.

The Raman spectra of glasses in the composition region $0.61 \leq x \leq 0.75$ are shown in figure 7. It is quite clear that the bands at 630 , 755 , 820 and 1210 cm^{-1} , as well as, the ones at ca 550 and 940 cm^{-1} , show a systematic intensity decrease upon increasing x . Thus, the borate groups responsible for these bands are progressively destroyed at such high Na_2O content glasses. At the same time another feature at

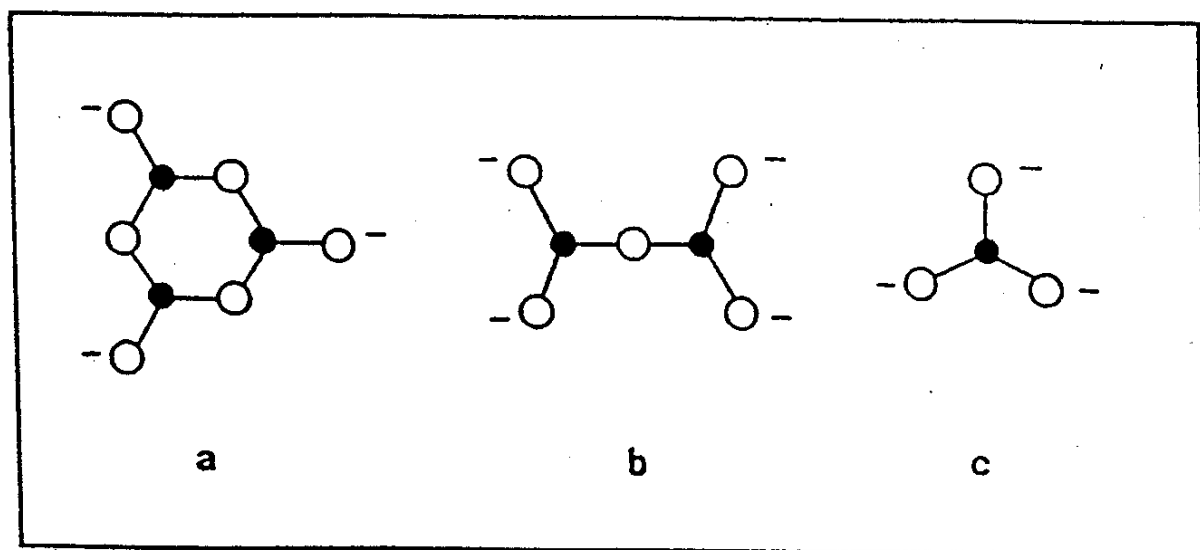


Fig. 6. Non-bridging oxygen containing borate units: metaborate ring (a), pyroborate (b) and orthoborate (c).

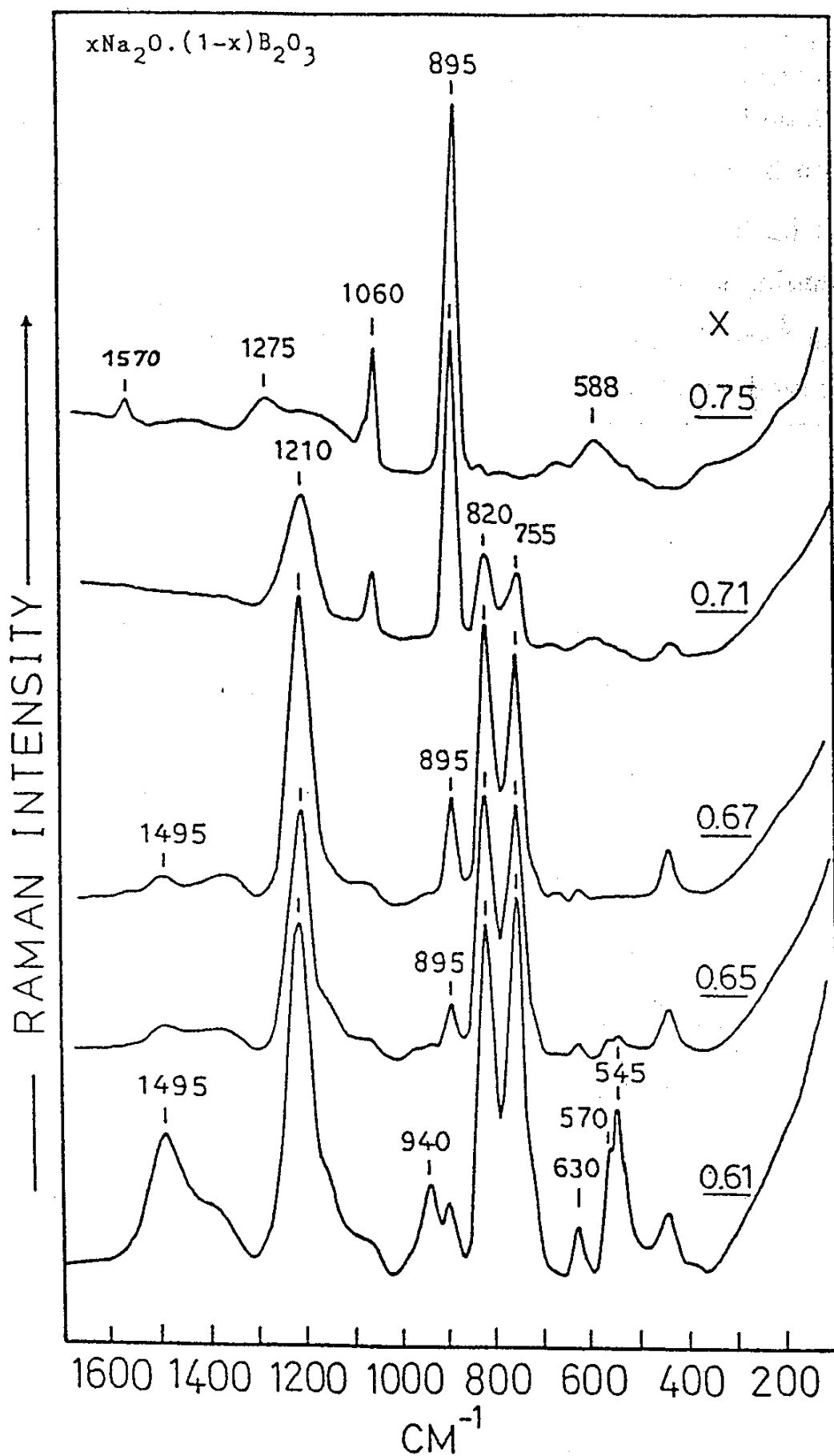


Fig 7. Raman spectra of $x\text{Na}_2\text{O} \cdot (1-x)\text{B}_2\text{O}_3$ glasses in the composition range $0.61 \leq x \leq 0.75$ [27].

pears at 895 cm^{-1} ($x=0.61$) and becomes the main band of the $x=0.75$ glass spectrum. We have attributed this band to orthoborate species (Fig. 6c), and specifically to the symmetric stretching vibration (ν_1) of BO_3^{3-} units (Fig.8). The weak band at 1275 cm^{-1} was assigned to the asymmetric stretching (ν_3) of BO_3^{3-} , and the one of 588 cm^{-1} to the in-plane bending mode (ν_4) of these units [27]. The weak band observed at 1570 cm^{-1} can be assigned to the overtone $2\nu_2$ of the out - of - plane bending mode ν_2 (Fig.8), which is infrared active only.

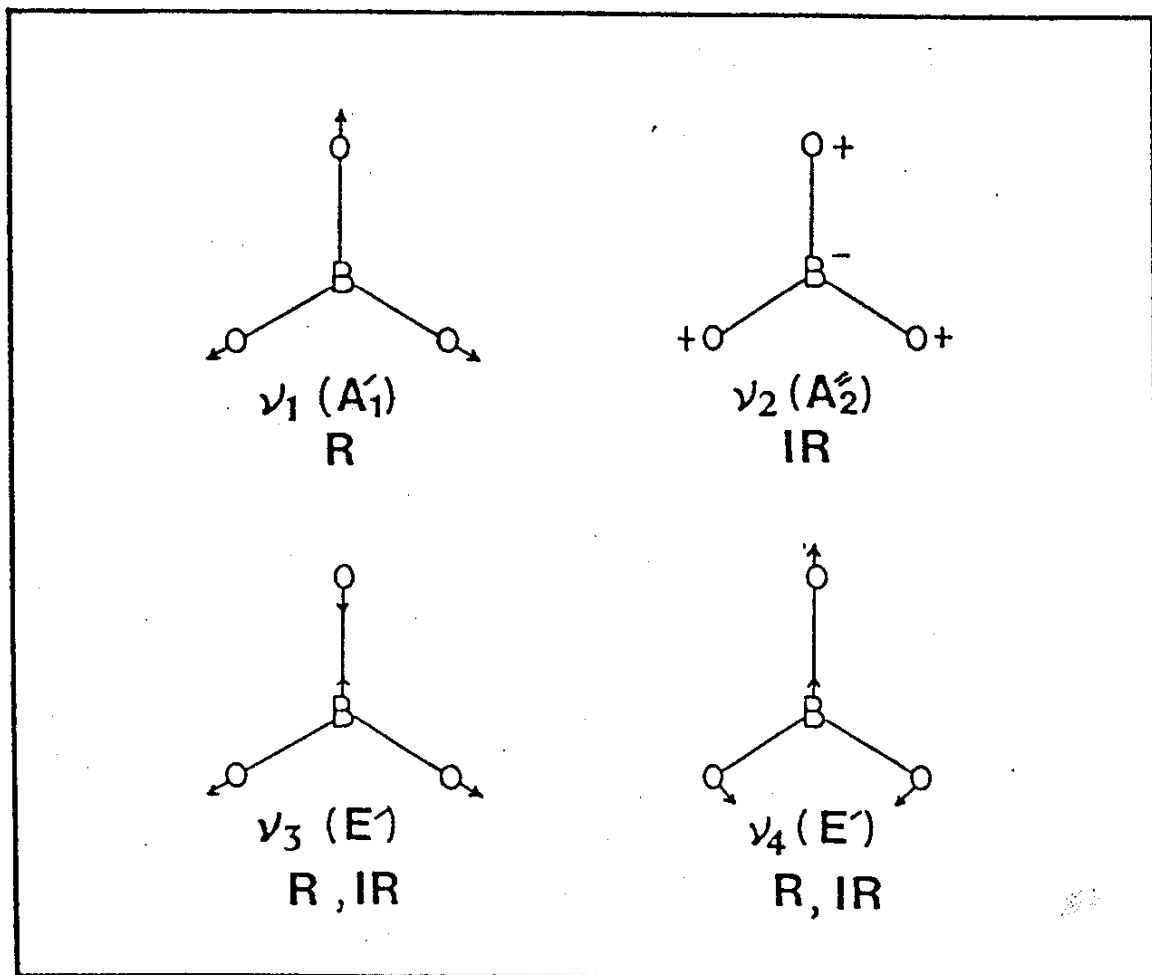


Fig. 8. Normal modes of vibration of planar BO_3^{3-} orthoborate units [28]. R and IR denote Raman and infrared activity respectively.

Besides the bands attributed to BO_3^{3-} species, the spectrum of the $x=0.75$ glass shows the existence of a sharp band at 1060 cm^{-1} , which was assigned to carbonate species (CO_3^{2-}) present in such "high - basicity" glasses. The influence of carbonates on the glass structure, their

interaction with the glassy environment, as well as their dependence on the time required for melting, temperature and composition have been recently investigated [29].

It can be concluded from the above presentation that Raman spectroscopy is an effective tool for probing the continuous variation of the network structure upon Na_2O addition. Thus, at low modification levels ($x \leq 0.30$) Na_2O causes the formation of four-coordinated boron atoms, which provide additional crosslinks to the borate network. At higher Na_2O - contents (0.35 - 0.55) the network is depolymerized through formation of non-bridging oxygen - containing units, like metaborate rings and pyroborates. At even higher sodium contents the latter units are decomposed in favour of the small and highly charged orthoborates. A return to a boron coordination of three is thus, possible at high x values.

The various borate units present in Na - borate glasses as a function of the Na_2O content are shown in figure 9, which was derived from the analysis of the Raman spectra [27].

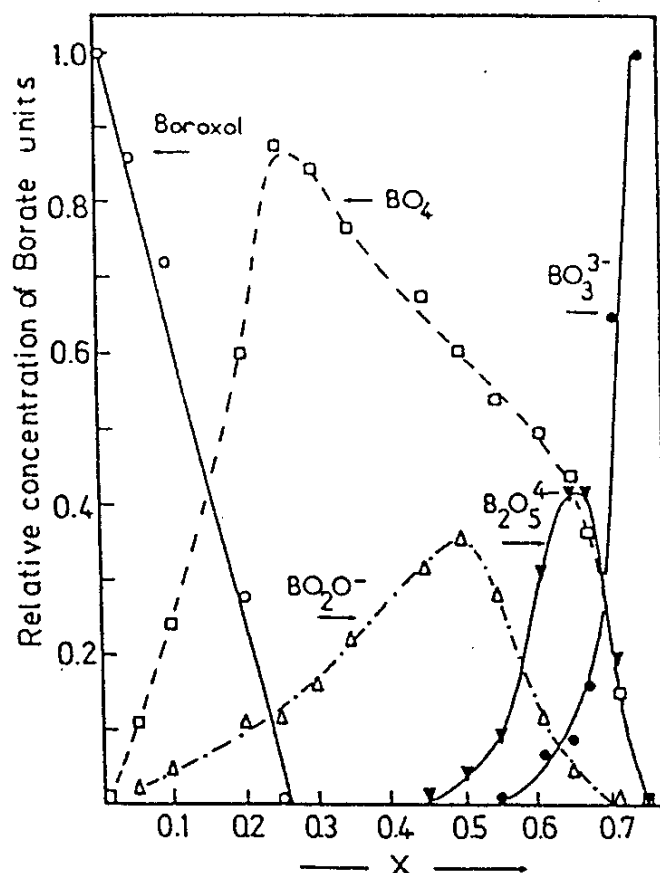


Fig. 9. Relative concentrations of some characteristic borate units in Na-borate glasses versus Na_2O content (x). BO_4 and BO_2O^- denote borate units containing BO_4 tetrahedra, and trigonal borons with one B-O bond respectively [27].

Among others, the compositional dependence of the relative concentration of BO_4 - containing units is of interest, since they are related to the rigidity of the borate network, as this is manifested through various physical properties of these glasses. Thus, we compare, in figure 10, the relative concentration of BO_4 - containing units with N_4 values [30], glass transition temperature, T_g , [31] and thermal expansion coefficient [32]. There is a good agreement between N_4 and relative concentration of BO_4 units, both exhibiting a maximum value at about 25 mol % Na_2O . Also, T_g goes through a maximum at approximately the same composition, manifesting a similar variation of network rigidity. The decrease of T_g upon increasing x ($x > 0.30$) is a consequence of the formation of non - bridging oxygen and thus network disruption. The thermal expansion coefficient shows a behavior opposite to that of T_g , since it is inversely related to network rigidity. It is thus quite clear that the so - called "borate anomaly" effect, exhibited by properties such as the T_g of the thermal expansion coefficient, is not really an anomaly, but rather a direct manifestation of the glass structural changes with metal oxide content. The composition dependence of other glass properties, such as the activation energy of ionic conductivity, can also be understood on the basis of the structural variations of these glasses [27].

ALKALI ACTION DEPENDENCE ON THE BORATE GLASS STRUCTURE

Previous studies of alkali borate glasses have indicated that the network structure is almost independent of the nature of the modifying action [21]. However, recent spectroscopic studies such as NMR [26] and far - infrared [33] have shown a considerable action effect on the glass structure. In this section we investigate whether Raman spectroscopy is capable of revealing the possible effect of alkali action on glasses having the same M_2O content.

Figure 11 shows the Raman spectra of Li - and Cs - borate glasses, for three representative compositions: $x = 0.17$, 0.40 and 0.50 [34]. A comparison of the spectra of glasses with the same x value shows pronounced differences, indicating the existence of network structural variation. The Li - borate glasses are composed of well interconnected borate units, such as six - membered rings with BO_4 tetrahedra (765 cm^{-1}) and diborate groups (1150 , 900 and 500 cm^{-1}), which take part in the formation of a rigid borate network [34]. The concentration of non - bridging - oxygen - containing units is small, considering the weak bands

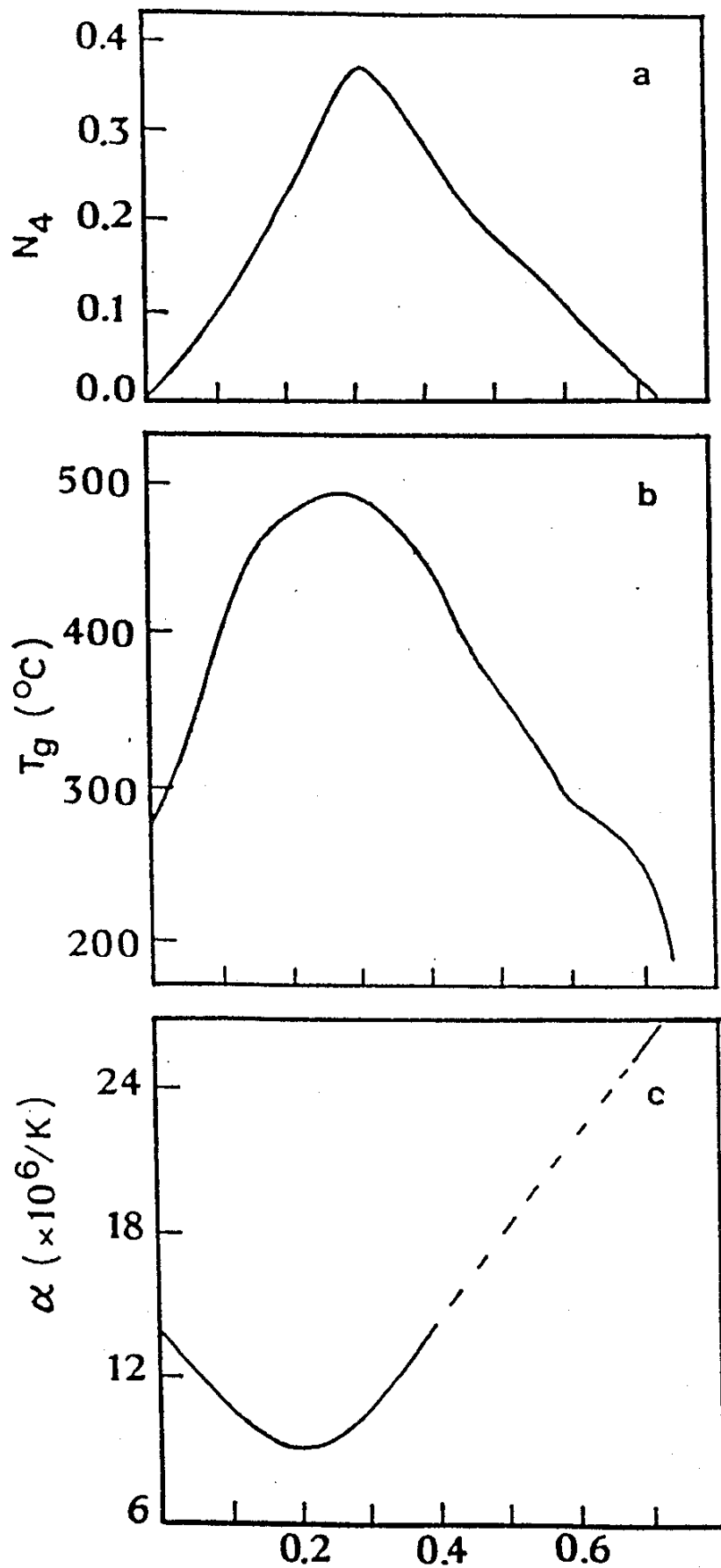


Fig. 10. Comparison of the compositional dependence of: (a) fraction of four coordinated boron atoms N_4 [30]; (b) glass transition temperature T_g [31], and (c) thermal expansion coefficient α , [32], for sodium - borate glasses.

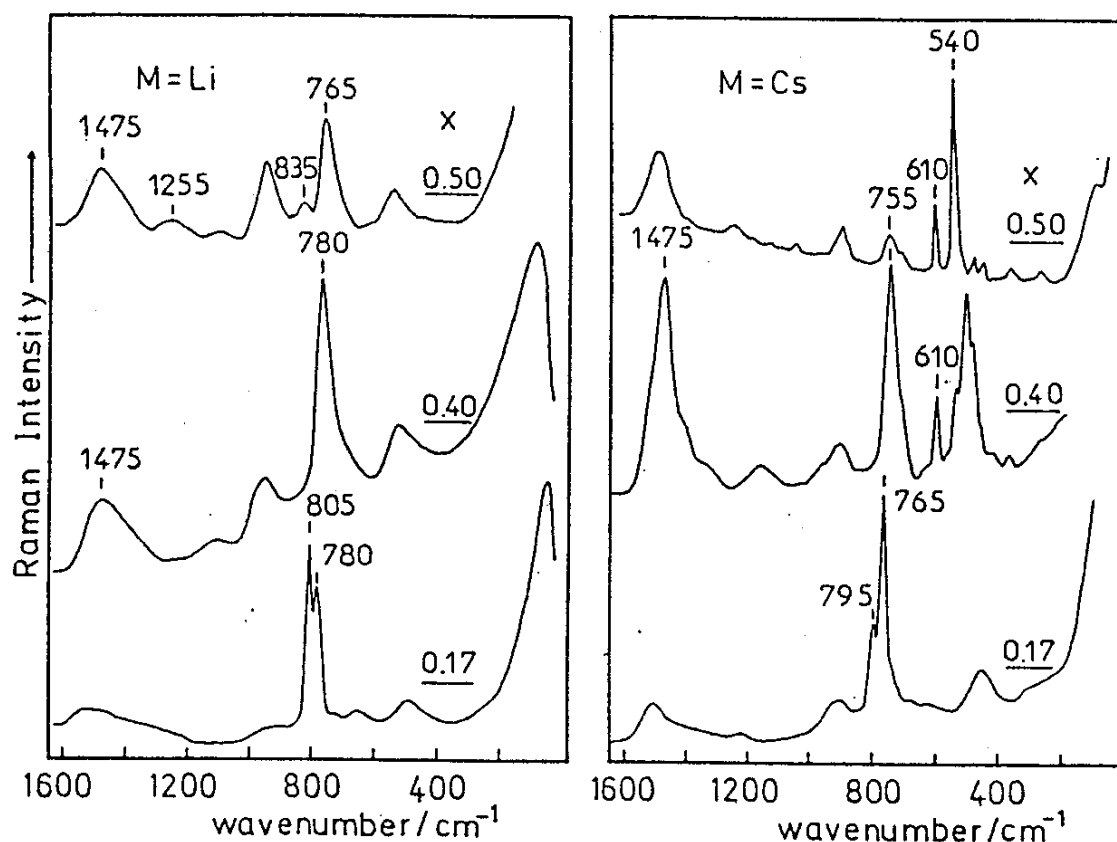


Fig. 11. Raman spectra of Li- and Cs-borate glasses for compositions $x=0.17$, 0.40 , 0.50 , [34,35].

at tributed to pyroborate units (820 and 1255 cm^{-1}) in the $x=0.50$ Li-glass spectrum. The spectra of Cs-glasses show the presence of a minor concentration of BO_4 -containing units, a high concentration of "loose" BO_4 tetrahedra (545 and 900 cm^{-1}) and non-bridging-oxygen-containing metaborate rings (610 cm^{-1}) [20].

This spectroscopic evidence indicates that the nature of the alkali action plays an important role in the determination of the structural units from which the network itself is composed. A systematic Raman and infrared study of all alkali borate-glass systems is in progress, in order to elucidate the details of the network structure and the nature of the action-network interactions relevant to the ion conduction.

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