CHAPTER 5

LASER RAMAN STUDIES ON QUARTERNARY GLASS SYSTEMS
CaO-B₂O₃-Al₂O₃-Na₂O AND CaO-B₂O₃-Al₂O₃-Fe₂O₃
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5.1. Introduction

Amorphous materials are characterized by the absence of long-range order in the arrangement of atoms and their structure is generally described in terms of a short-range order. Structural studies of glasses have been carried out using different experimental techniques[1-5]. Laser Raman spectroscopy has been widely used for the investigation of structure of different types of glasses[6-10]. Particularly, a number of investigations on borate glasses have been reported[11-15]. A comprehensive review of Raman studies on borate glasses has been published by Konijnendijk and Stevels[11]. Very recently, Meera and Ramakrishna have reviewed the later studies on these type of glasses[12].

In this chapter, the author presents laser Raman studies on the quarternary glass systems CaO-B₂O₃-Al₂O₃-Na₂O and CaO-B₂O₃-Al₂O₃-Fe₂O₃. A brief review of the Raman studies on borate glasses is also included in this chapter.
5.2. A Short Review

As pointed out by Konijnendijk et al.[11], the interpretation of Raman spectra of borate glasses is not straightforward and usually information on the structural units present in different glass systems is obtained by comparison of the Raman spectra of the glasses with those of borate compounds whose crystal structure is known. This is based on the assumption that structural units or groups in glasses resemble the units or groups in comparable compounds[11,13]. The structure of glasses has been the topic of many theoretical investigations[14,15]. Two basic approaches viz., random network hypothesis[16,17] and the crystallite model[17] have been proposed for the description of structure of disordered materials[12]. According to the first hypothesis the fundamental polyhedra present in crystals (e.g., SiO$_4$ in SiO$_2$ crystals) exist as such as in the corresponding glasses. These polyhedra are connected together by allowing some degree of bond angle distortion and more or less complete freedom for value of dihedral angles. This theory has been applied with considerable success to explain the structure of amorphous Si, Ge and As. According to the second hypothesis a glass consists of submicroscopically ordered regions which are connected together by a disordered structure. But this model does not enjoy much experimental support[12].
The structure of borate glasses is best described by the group model primarily suggested by Krog-Moe[18]. This model is based on the assumption that structural units or groups present in oxide melts or oxide glasses resemble the units or groups present in the corresponding crystalline compound. In the analysis of Raman spectra of borate glasses, the Raman spectra of crystalline compounds are used as the finger prints for the identification of specific groups in the corresponding glasses. The different types of borate groups presently known are given in figure 1.10 (Chapter 1)[11]. The structural and physical properties of B₂O₃ glasses have been investigated by many workers[11,19-30]. The main feature of the Raman spectrum of B₂O₃ glasses is a narrow, intense and strongly polarized band centered at 806 cm⁻¹[25,25a,16,33]. Mozzie and Warren[31] from X-ray diffraction experiments have shown that vitreous B₂O₃ is primarily built up of boroxol ring which are linked together, and a small number of BO₃ unit, which are not part of the boroxol rings, linked randomly to the boroxol groups. This was also suggested by other workers[21a]. This conclusion was based on the fact that the strongest peak in the Raman Spectra of B₂O₃ glasses at 806 cm⁻¹ coincide with a strong Raman peak in several boroxol derivatives. Since this peak is strongly polarized it must be due to a totally systematic vibration. Parsons[32] and Krogh-
Moe[21] attributed this peak to a trigonal deformation of the boroxol ring. This suggestion has also been supported by the theoretical calculation of the vibrational spectra of boroxol groups with different groups attached to the boroxol ring[33]. In contrast with the Raman spectrum of vitreous $\text{B}_2\text{O}_3$, the Raman spectrum of crystalline $\text{B}_2\text{O}_3$ does not have a peak at $806 \text{ cm}^{-1}$ indicating the absence of boroxol rings[34]. Crystal structure of crystalline $\text{B}_2\text{O}_3$ has been shown to consist of BO$_3$ triangles and not boroxol rings[35].

The Raman spectra of $\text{B}_2\text{O}_3$ glasses have also been reported to be characterized by a weak and broad band centered around $1260 \text{ cm}^{-1}$[22,28,29,30]. This band has been reported to be originating from the delocalized B-O stretch involving both the ring and network contribution[28]. The band has the characteristics of a Continuous Random Network (CRN) mode[30] indicating that $\text{B}_2\text{O}_3$ glass is made up of continuous random network of boroxol rings.

The Raman spectra of vitreous $\text{B}_2\text{O}_3$ undergo pronounced change on the addition of other oxides like alkali oxide, alkaline earth oxide, combination of alkali oxides and alkaline earth or $\text{Al}_2\text{O}_3$. The Raman spectra of binary
alkali borate glasses: $x R_2O-(1-x)B_2O_3$ (R=Li, Na, K, Rb, Cs) containing up to 70 mol% of alkali oxide have been extensively studied by many researchers\[11,23,26,36-43\]. The Raman spectra of alkali borate glasses containing different alkali ions show a close resemblance\[11,12\]. The most prominent characteristic of binary alkali borate glasses for low concentration of alkali oxide is the peak at 806 cm$^{-1}$. Upon increasing the alkali oxide content the intensity of this peak of 806 cm$^{-1}$ decreases and a new peak starts developing at about 770 cm$^{-1}$. At 20 mol% of alkali oxide the 806 cm$^{-1}$ peak appears only as a shoulder of 770 cm$^{-1}$ peak and in the case of sodium and cesium borate glasses the 806 cm$^{-1}$ peak completely disappears at a concentration of 25 mol% of the alkali oxide\[11,12\]. As the alkali oxide concentration increases beyond 30 mol%, the peak at 770 cm$^{-1}$ shifts towards lower frequency. At alkali oxide concentrations in the range 20-35 mol%, the strongest peak is observed in the range 770-755 cm$^{-1}$.

Since 806 cm$^{-1}$ peak is characteristic of the boroxol group, it is obvious that on the addition of alkali oxide to boron oxide, the boroxol groups are converted into other groups. Also, the disappearance of the 806 cm$^{-1}$ peak at about 25 mol% of alkali oxide indicates that vitreous boron oxide structure is not made up of random network of $BO_3$ triangles, since at 25 mol% alkali oxide
not all these BO₃ triangles with three bridging oxygen ions can be converted into other types of groups[11]. From the studies of binary sodium and potassium borate glasses, Konijnendijk[11] has shown that the peak which arises at about 770 cm⁻¹ is due to a symmetric breathing vibration of a six-membered borate ring with one BO₄ tetrahedra[24]. Through a comparison of the Raman spectra of sodium and potassium borate glasses containing 20 mol% alkali oxide with the spectra of various alkali borate compounds, Konijnendijk has concluded that tetraborate groups, that is, a couple consisting of one pentaborate and one triborate group are formed in the concentration range 0-20 mol% alkali oxide at the expense of boroxol rings. This conclusion was also confirmed by IR spectra, X-ray analysis, NMR studies and melting point depressions[18,24,44,45].

Konijnendijk has also concluded that in the composition range 20-35 mol% alkali oxide, the tetraborate groups are gradually replaced by diborate groups upon increasing the alkali oxide content. At about 33 mol% of alkali oxide, the network is built up mainly of diborate groups with minor number of loose BO₃ triangles, loose BO₄ tetrahedra with ring-type metaborate groups probably also present. This picture has also been confirmed by the NMR measurements of Rhee and Bray[45]. Konijnendijk has
assigned the peak at 755 cm\(^{-1}\) to diborate groups. Raman spectra of alkali borate glasses with high alkali content contain a peak at 755 cm\(^{-1}\). Brii[24] has attributed this peak to the presence of dipentaborate groups which result from the incorporation of a second BO\(_4\) tetrahedron into a pentaborate group. (i.e., this peak arises out of the presence of groups containing two BO\(_4\) tetrahedra). For still higher concentration of alkali oxide, loose diborate and loose BO\(_4\) groups giving rise to a peak around 500 cm\(^{-1}\) are also formed. The peak at 560 cm\(^{-1}\) in the case of alkali concentration of about 50 mol% has not been conclusively assigned by Konijnendijk, though he tentatively assigned the peak to isolated diborate groups. The peaks at 630, 730, 820 and 940 cm\(^{-1}\) in glasses containing alkali oxide concentration between 40 and 50 mol% have been attributed to groups containing non-bridging oxygen viz., pyroborate groups (B\(_2\)O\(_5\))\(^{4-}\) and orthoborate units (BO\(_3\))\(^{3-}\), ring type metaborate and chain type metaborate groups from a comparative study of spectra of these glasses with those of compounds containing these groups[11]. The presence of a peak at 760 cm\(^{-1}\) in the spectra of glasses containing up to about 50 mol% of alkali oxide is attributed to the presence of a significant number of BO\(_4\) units, probably in diborate groups.
Recently the assignments of the peak centered at 755 cm\(^{-1}\) by Konijnendijk\[11\] has been questioned by Irion et al.\[37\]. Krogh-Moe\[46\] and Matinez-Ribll et al.\[41\] studied the Raman spectra of zinc diborate and lithium diborate which contain diborate groups, and observed no peak at 755 cm\(^{-1}\) in the spectrum of either material but observed peaks around 1050, 980 cm\(^{-1}\) for ZnO-2B\(_2\)O\(_3\) and at 1035, 930 and 980 cm\(^{-1}\) for Li\(_2\)O-2B\(_2\)O\(_3\). It is now well accepted that diborate groups are identified by the presence of a peak around 1100 cm\(^{-1}\)\[37,41-43,12\]. In a very recent review Meera et al.\[12\] have indicated that only the simultaneous occurrence of peaks around 930, 770, 650 and 500 cm\(^{-1}\) is a reliable indication of the presence of pentaborate groups. Thus it appears that in alkali borate glasses containing upto 25 mol\% of alkali oxide, boroxol rings are converted to pentaborate groups and not to tetraborate or triborate groups\[11\].

Raman spectra of binary borate glasses containing alkaline-earth ions with general formula RO:B\(_2\)O\(_3\) for R=Ba, Ca, Sr, Mg and Pb have been reported\[23,40,48,49\]. In Raman spectra of 0.20 BaO-0.80 B\(_2\)O\(_3\), the most prominant peak is the one at 775 cm\(^{-1}\) and peak at 806 cm\(^{-1}\) is totally absent. This indicates that in this glass no boroxol groups are present and all the BaO is used for the formation of BO\(_4\) units. It may be thought that the BO\(_4\)
tetrahedra are connected to each other, so that one \( \text{Ba}^{2+} \) ion can compensate for the negative charge of two \( \text{BO}_4 \) units close to one another[11,12]. It has been concluded that it is reasonable to consider the borate network in the 0.20 \( \text{BaO}-0.80 \text{B}_2\text{O}_3 \) glasses to be consisting primarily of tetraborate groups[12]. The peaks at 930, 650 and 485 cm\(^{-1}\) in the Raman spectra of this glass show the existence of pentaborate groups. In Raman spectra of binary glasses containing 30 mol% alkaline-earth (Ba, Ca, Sr), the most prominent peak appears at around 755 cm\(^{-1}\) showing close similarity to the Raman spectra of alkali borate glasses. However, in the Raman spectra of 30 mol% barium and calcium borate glasses the high frequency band appears to be more intense and occurs at a lower frequency (1300 cm\(^{-1}\)) than in the alkali borate glasses[12]. Detailed study of the glass system \( x \text{MgO-} (100-x) \text{B}_2\text{O}_3 \) over its glass forming region has been reported[40,12]. The prominent peaks for different values of \( x \) are at 806 cm\(^{-1}\) and 785 cm\(^{-1}\) for \( x > 44.4 \) mol\%, and 785 cm\(^{-1}\) and 690 cm\(^{-1}\) for \( x=50 \) mol\%[12]. Raman studies of binary borate glasses containing cations other than alkaline earths have been reported in systems \( \text{RO-B}_2\text{O}_3 \) with \( R = \text{Cd}, \text{Pb}, \text{Bi}, \text{Zn}, \text{Si} \) and \( \text{Ge}[48,50,51,52,53,54] \). In cadmium borate glasses, the 806 cm\(^{-1}\) peak due to boroxol rings is present for glasses containing as much as 42.8 mol\% \( \text{CdO} \). Also the spectrum contains a peak centered
around 775 cm\(^{-1}\), which decreases in intensity and shifts to lower frequency as the CdO content increases. The simultaneous presence of peaks at 775, 945, 640 and 510 cm\(^{-1}\) indicates the presence of pentaborate groups in these glasses. The shift towards lower frequency of the 775 cm\(^{-1}\) peak with increase in the concentration of CdO shows the formation of dipentaborate groups. The band around 1100 cm\(^{-1}\) corresponding to the diborate groups is present in the spectrum for the range of composition from 33.3 mol\% to 52.4 mol\% of CdO\(^{48,12}\). CdO is both a network former and a network modifier. The slower consumption of boroxol rings in cadmium borate glasses is due to the formation of diborate groups (i.e., groups with connected \(\text{BO}_4\) units) as well as due to incorporation of CdO in the network as network former. An interesting feature of the cadmium borate glasses is the presence of the intense high frequency band centered around 1390 cm\(^{-1}\) which is assigned to B-O vibrations occurring in large borate network\(^{12,48,55}\). The high intensity of this band suggests that the CdO is less capable (compared to alkali and magnesium ions) of breaking the network into smaller groups like pyroborate and orthoborate but results in the formation of non-bridging oxygens connected to large borate network\(^{12,48}\).
The Raman spectra of xZnO-(100-x)B₂O₃ for x between 50 and 65 mol% show no significant changes with increase in the ZnO concentration[12,51]. The spectra consists only of broad bands and the nature of the spectra does not improve on annealing the glasses[12]. The Raman results support the network forming tendency of ZnO but its role in network modification is not clearly known[12].

The replacement of an alkali oxide by another alkali oxide in borate glasses is reported to cause a non-linear variation in their physical properties. This effect known as mixed alkali effect has also been reported in the Raman study of glasses[56]. The ratio of the intensity of the 770 cm⁻¹ peak to that of 806 cm⁻¹ peak is observed to be greater in the binary calcium borate glasses than in the binary lithium borate glasses[56]. But, when Li₂O is replaced by Cs₂O, the intensity ratio I₇₇₀/I₈₀₆ does not vary linearly. For a given amount of total alkali content a distinct minimum is observed in the I₇₇₀/I₈₀₆ Vs CS₂O/(CS₂O + Li₂O) behaviour. The result has been explained on the basis of weak electrolyte model[57,58]. According to this model, mixed alkali effect is due to the preferential formation of mixed alkali pairs resulting in the formation of non-bridging oxygens. The formation of non-bridging oxygens destroys the six-membered rings resulting in the decrease of 770 cm⁻¹ peak[12,56].
Raman spectra of ternary glass system \( \text{CaO-Na}_2\text{O-B}_2\text{O}_3 \) is reported to be similar to that of binary sodium borate containing the same amount of \( \text{B}_2\text{O}_3 \)[59]. But the behaviour of \( \text{MgO-Na}_2\text{O-B}_2\text{O}_3 \) glass is reported to be different[40,59].

Another important glass system reported to have been studied using Raman spectroscopy in ternary systems containing \( \text{Al}_2\text{O}_3 \). The effect of incorporation of \( \text{Al}_2\text{O}_3 \) in alkali and alkaline-earth borate glasses has been investigated by many workers[11,60]. In glasses of composition \( \text{K}_2\text{O}-80 \text{B}_2\text{O}_3 \), incorporation of \( \text{Al}_2\text{O}_3 \) of concentration from 10 to 20 mol\% results in an increase of the intensity of the 806 cm\(^{-1}\) band and a decrease of the peak at 770 cm\(^{-1}\) in the Raman spectra. Addition of 20 mol\% of \( \text{Al}_2\text{O}_3 \) results in the disappearance of 770 cm\(^{-1}\) peak. This indicates that the addition of \( \text{Al}_2\text{O}_3 \) leads to a decrease in the number of \( \text{BO}_4 \) tetrahedra, and boroxol groups are formed again. \( \text{Al}_2\text{O}_3 \) is probably incorporated in the structure as \( \text{AlO}_4 \) units. The oxygens of \( \text{Na}_2\text{O} \) do not convert \( \text{BO}_3 \) units to \( \text{BO}_4 \) units but get used up for the formation of \( \text{AlO}_4 \) tetrahedra[11,60]. However, no Raman peaks corresponding to \( \text{AlO}_4 \) tetrahedra are observed in the Raman spectra[11,60]. Similar results have also been reported for \( \text{MgO-Al}_2\text{O}_3\cdot\text{B}_2\text{O}_3 \) glasses[11]. Raman studies of ternary alkali borosilicate and borogermanate glasses have also been reported [11,61,62].
Raman spectra of quarternary glasses have not been extensively studied. The latest review of Raman studies of borate glasses does not indicate such studies on quarternary glasses.

5.3. Work Undertaken in the Present Study

The author reports the study of Raman spectra of the quarternary glass systems Na₂O-CaO-B₂O₃-Al₂O₃ and Fe₂O₃-CaO-B₂O₃-Al₂O₃ in this chapter. It was found that the Raman scattering is poor in the CaO-B₂O₃-Al₂O₃-Fe₂O₃ glass system. The effects on the Raman bands of the variations in the concentrations of Na₂O, CaO, Al₂O₃ and Fe₂O₃ were investigated. For comparison, the laser Raman spectrum of cabal glass CaO-B₂O₃-Al₂O₃ had also been recorded. The band corresponding to the boroxol units at 806 cm⁻¹ [11,12] is absent in the spectra of the glass system CaO-B₂O₃-Al₂O₃-Na₂O while weak scattering corresponding to this band is present in some of the spectra of the glass system CaO-B₂O₃-Al₂O₃-Fe₂O₃. But peaks corresponding to other borate groups viz., pentaborate, diborate, etc. are present in all the spectra.
5.4. Experimental Details

The procedure for the preparation of the samples are described in Section 3.7 of Chapter 3. Glass samples of thickness about 1 mm were chosen for the Raman studies. The spectra were recorded at room temperature in the stokes region using Dilor Z 24 Raman spectrometer using the 488 nm line of the Ar⁺ laser as the exciting radiation and with a power of about 70 mW incident on the samples. The scattered radiation was measured at an angle of 90° from the incident laser beam.

5.5. Results and Discussion

The laser Raman spectrum of the cabal glass CaO-B₂O₃-Al₂O₃ and the spectra of the glass systems CaO-B₂O₃-Al₂O₃-Na₂O and CaO-B₂O₃-Al₂O₃-Fe₂O₃ for different concentrations of the components are shown in figure 5.1 to 5.13. The spectra of the different systems of glasses are discussed in the following sections.

(i) CaO-B₂O₃-Al₂O₃ (cabal) glass system

The laser Raman spectrum of the cabal glass system for a typical composition of 20CaO-65B₂O₃-15Al₂O₃ is shown in figure 5.1. The most prominent feature of the spectrum
is the broad band centered around 795 cm\(^{-1}\). It has been reported\([11,20,21,29]\) that the most prominent feature of the Raman spectrum of vitreous B\(_2\)O\(_3\) is a sharp band centered around 806 cm\(^{-1}\) and that when an alkali oxide is added to B\(_2\)O\(_3\), the intensity of the peak at 806 cm\(^{-1}\) decreases and another peak develops at 770 cm\(^{-1}\). The 806 cm\(^{-1}\) peak disappears for alkali oxide concentration of about 20 mol\%. The 806 cm\(^{-1}\) peak has been assigned to boroxol rings by Bril et al.\([24]\) and others\([11,12]\). In the present study the peak at 795 cm\(^{-1}\) which is close to 806 cm\(^{-1}\) may be assigned to boroxol rings. Konijnendijk had assigned at 770 cm\(^{-1}\) to tetraborate groups formed at the expense of boroxol rings. But the assignment of the 770 cm\(^{-1}\) peak to tetraborate groups has been indicated to be ambiguous by Meera et al.\([12]\). These authors have pointed out that both triborate and tetraborate groups give rise to the 770 cm\(^{-1}\) band and a weak band at 930 cm\(^{-1}\) but no band in the 660 cm\(^{-1}\) region. Hence the 770 cm\(^{-1}\) band alone cannot be taken to indicate the presence of a particular groups. Meera et al.\([12]\) has also indicated that the simultaneous occurrence of peaks around 930, 770, 650 and 500 cm\(^{-1}\) is a reliable proof of the presence of pentaborate group. In the present study, the band around 940 cm\(^{-1}\), 480 cm\(^{-1}\) and the shoulder around 770 cm\(^{-1}\) together with noticeable scattering around 650 cm\(^{-1}\) may be attributed to pentaborate groups. From the prominence of
the peak at 795 cm\(^{-1}\) it may be inferred that the structure of the glass is made up of a continuous random network of boroxol rings. It may also be inferred that the boroxol rings have started transformation into pentaborate group at the composition 20CaO-65B\(_2\)O\(_3\)-15Al\(_2\)O\(_3\). Brill[24] had shown that a peak around 500 cm\(^{-1}\) corresponds to loose diborate and loose BO\(_4\) groups. In figure 5.1 the broad peak centered around 480 cm\(^{-1}\) which is close to 500 cm\(^{-1}\) may be considered to be an indication of these groups. The peaks around 1100 cm\(^{-1}\) may be attributed to diborate groups in comparison with reported results[12,37,41-43]. The band centered around 1436 cm\(^{-1}\) may be assigned to B-O vibrations occurring in large borate network in comparison with the band around 1390 cm\(^{-1}\) in cadmium borate[52,59] and other borate glasses[12]. It has been reported that Raman spectra of binary borate glass system RO:B\(_2\)O\(_3\) (R= Ba, Ca, Sr) containing about 30 mol\% of RO, are dominated by a band at 755 cm\(^{-1}\) due to dipentaborate groups. In the present study even though the combined concentration of CaO and Al\(_2\)O\(_3\) exceeds 30 mol\%, there is no identifiable band but only a weak scattering around 755 cm\(^{-1}\) indicating the lack of a large percentage of dipentaborate groups.

In comparison with the reported spectra of binary and ternary glasses[11,12], it may be concluded that the
structure of the cabal glass with composition 20CaO-65B₂O₃-15Al₂O₃ consists mainly of a continuous random network of boroxol rings. Small percentages of pentaborate and diborate groups and loose diborate and loose BO₄ groups are also present in the glass. The broad peak of appreciable intensity around 1436 cm⁻¹ is a strong indication of continuous random network. The addition of CaO and Al₂O₃ (total concentration 35 mol%) does not break the network into smaller groups like pyroborate and orthoborate. This factor may be considered to be contributing to the large intensity of the 795 cm⁻¹ peak (which is closed to 806 cm⁻¹) in the present study.

(ii) CaO-B₂O₃-Al₂O₃-Na₂O glass system

(a) Variation of concentration of Na₂O

The Raman spectra of the quartenary glass system CaO-B₂O₃-Al₂O₃-Na₂O for two different concentrations of Na₂O (15 and 24 mol%) are given in figure 5.2 and 5.3. The most prominent peak in the spectrum for lower concentration of Na₂O is a broad and intense peak centered around 783 cm⁻¹ where as this peak around 778 cm⁻¹ has much lower intensity in the spectrum of the glass with higher concentration of Na₂O. In the present study it may be inferred that the glass of composition 10CaO-60B₂O₃-15Al₂O₃-15Na₂O is mainly built up of tetraborate groups.
and as the concentration of Na₂O is increased to 24 mol%, the tetraborate groups convert to diborate groups. The much reduced intensity of the 778 cm⁻¹ band in the spectrum for larger concentration of Na₂O (figure 5.3) clearly shows that the glass is not made up of mainly tetraborate groups.

Meera et al.[12] have reported that the presence of pentaborate groups may be concluded from the simultaneous occurrence band at 770, 930 and 616 cm⁻¹ along with the considerable scattering in the 500 cm⁻¹ region. In figure 5.2 the shoulder around 770 cm⁻¹, in the band centered around 915 cm⁻¹ (close to 930 cm⁻¹) and the weak band at 673 (close to 666) cm⁻¹ along with considerable scattering around 481 cm⁻¹ may be considered to be an indication of pentaborate groups. In figure 5.3 the scattering in the region 472 cm⁻¹ is the most prominent feature of the spectrum and this along with appreciable scattering around 770 cm⁻¹ and 670 cm⁻¹ and the band centered around 918 cm⁻¹ may be interpreted as an indication of the predominance of pentaborate group in the structure of the glass containing larger mol% of Na₂O (24 mol%). In comparison with the reported results[16,17] the weak bands around 1000 cm⁻¹ in figure 5.2 and that around 1040 cm⁻¹ in figure 5.3 may be assigned to diborate group which might have resulted from
the conversion of a few tetraborate group to diborate group. The bands around 481 cm⁻¹ in figure 5.2 and 472 cm⁻¹ in figure 5.3 when interpreted independently (from the band at 783, 915 and 673) leads to the conclusion that the glass system with the lower (15 mol%) as well as higher (24 mol%) Na₂O concentration contain loose diborate group and loose BO₄. The high frequency band around 1443 cm⁻¹ for lower and around 1436 cm⁻¹ for higher concentration Na₂O indicate the presence of B-O vibrations occurring in a large borate network[11,12]. The lower intensity of the high frequency band shows that at higher concentration (24 mol%) of Na₂O smaller groups such as pyroborate and orthoborate are predominantly present in the structure of the glass.

Comparing figure 5.2 and 5.3 with figure 5.1 it may be seen that the addition of a fourth component (Na₂O in this case) does not affect the structure of the glass to a great extent.

(b) Variation of concentration of CaO

The spectra for the glass system CaO-B₂O₃-Al₂O₃-Na₂O containing two different concentrations of CaO are given in figure 5.4 and 5.5. For lower CaO content (5 mol%) the most prominent feature of the spectrum (figure 5.5) is a
narrow band around 798 cm\textsuperscript{-1}. This band is very close to band corresponding to the boroxol rings (806 cm\textsuperscript{-1}) and hence indicates the predominance of the boroxol rings in the structure of glass. A band around 770 cm\textsuperscript{-1} also appears as a shoulder on the low frequency side of the 798 cm\textsuperscript{-1} band indicating that other groups have started to develop at the expense of boroxol groups. The simultaneous presence of shoulder around 770 cm\textsuperscript{-1}, the bands around 458 and 650 cm\textsuperscript{-1} and the weak band around 900 cm\textsuperscript{-1} is an indication of a small percentage of pentaborate group. The broad peak around 485 cm\textsuperscript{-1} indicates the presence of diborate and loose BO\textsubscript{4} groups\cite{17}. The band around 1460 cm\textsuperscript{-1} must be due to delocalized B-O stretches\cite{17}. The presence of the weak band 650 cm\textsuperscript{-1} indicates ring type metaborate groups.

When the concentration of CaO in the glass system is increased to 15 mol\%, conspicuously different features develop in the spectrum. The most prominent peak is around 770 cm\textsuperscript{-1} while there is no peak around 800 cm\textsuperscript{-1}. Another conspicuous feature of figure 5.5 in comparison with figure 5.4 is the existence of broad, somewhat intense peak around 910 cm\textsuperscript{-1}. The strongest peak at 773 cm\textsuperscript{-1} together with the peaks around 910 and 473 cm\textsuperscript{-1}, and weak band around 650 cm\textsuperscript{-1} may be attributed to pentaborate groups. This clearly shows that as the
concentration of CaO is increased, the boroxol rings convert into pentaborate group and at a concentration < 15 mol% of CaO all the boroxol rings have undergone this transformation. From a comparison of figure 5.4 and figure 5.5, it may be noted that the features representing pentaborate groups are stronger for larger concentration of CaO (figure 5.5) than for smaller concentration (figure 5.4) which indicates that at larger concentration of CaO, there is a larger concentration of pentaborate groups. The peak around 473 cm\(^{-1}\) is an indication of the existence of loose borate and loose BO\(_4\) group[12]. The larger intensity of the high frequency peak around 1460 cm\(^{-1}\) at higher CaO concentration (figure 5.5) shows the B-O vibrations occurring in a large borate network and leads to the inference that large concentration of CaO helps in maintaining the network without breaking into smaller groups.

(c) Variation of concentration of Al\(_2\)O\(_3\)

The main features of the spectrum of the glass system for lower concentration of Al\(_2\)O\(_3\) (figure 5.6) are a narrow strong peak around 765 cm\(^{-1}\) and a broad strong peak centered around 1473 cm\(^{-1}\). The peak around 765 cm\(^{-1}\) may be considered to be close to 770 cm\(^{-1}\). The strong band at 765 cm\(^{-1}\) together with bands around 950 and 650 cm\(^{-1}\), and
the weak band around 500 cm\(^{-1}\) may be attributed to pentaborate groups. The complete absence of a band around 806 cm\(^{-1}\) indicates that complete transformation boroxol rings into other groups like pentaborate groups has taken place. It has been reported that in the case of alkali borate glasses, the 806 cm\(^{-1}\) band completely disappears at about 25 mol\% concentration of alkali oxide. In the present case the complete disappearance 806 cm\(^{-1}\) band at a concentration 5 mol\% Al\(_2\)O\(_3\) in the glass system 10 CaO-5Al\(_2\)O\(_3\)-65B\(_2\)O\(_3\)-20Na\(_2\)O may be considered to be in agreement with the above result considering the fact that the total mol\% of additives (35 mol\%) to B\(_2\)O\(_3\) exceeds 25.

Also the broad but strong band around 1473 cm\(^{-1}\) is an indication of the predominance of B-O vibrations in the network which also shows that the network is maintained without breaking into smaller group.

The spectrum (figure 5.7) for larger concentration Al\(_2\)O\(_3\) (20 mol\%) in the glass system 10 CaO-50 B\(_2\)O\(_3\)-20Al\(_2\)O\(_3\)-20Na\(_2\)O appears very much different from that for lower concentration of Al\(_2\)O\(_3\) (figure 5.6) the strong and somewhat sharp band at 772 cm\(^{-1}\) is the prominent feature of the spectrum. The strong bands centered around 466 cm\(^{-1}\), around 950 cm\(^{-1}\) and the strongest band at 772 cm\(^{-1}\), and the scattering around 650 cm\(^{-1}\) which appears as a shoulder on the low frequency side of the band at 772 cm\(^{-1}\), may be attributed to pentaborate groups.
The prominence of all these bands indicates the strong concentration of pentaborate groups in the spectrum. The strong, broad band around 1420 cm\(^{-1}\) is assigned to B-O vibrations occurring in large borate network. The strong band around 465 cm\(^{-1}\) also indicates the presence of loose diborate and loose BO\(_4\) groups. Thus comparing figures 5.6 and 5.7 with the spectrum of alab glass (figure 5.1) it is seen that in the glass system containing Al\(_2\)O\(_3\) total conversion of boroxol groups into pentaborate groups has taken place. In addition it may be inferred that the borate network is maintained without breaking into smaller groups like pyroborate and orthoborate groups in the glass system containing Al\(_2\)O\(_3\).

(iii) CaO-B\(_2\)O\(_3\)-Al\(_2\)O\(_3\)-Fe\(_2\)O\(_3\) glass system

In the Raman scattering experiments it was found that the scattering of glasses containing Fe\(_2\)O\(_3\) is very poor. Hence Raman spectra of glasses containing only low concentration of Fe\(_2\)O\(_3\) had been recorded in the present study.

(a) Variation of concentration of Fe\(_2\)O\(_3\)

The laser Raman spectra of the glass system CaO-B\(_2\)O\(_3\)-Al\(_2\)O\(_3\)-Fe\(_2\)O\(_3\) for two different concentration of Fe\(_2\)O\(_3\) are
given in figure 5.8 and 5.9. The spectrum of the samples for lower concentration (2 mol%) of Fe$_2$O$_3$ (figure 5.8) consists of bands around 795, 442 and 1305 cm$^{-1}$. Also weak scattering is present in the regions around 650 and 900 cm$^{-1}$. The band around 795 cm$^{-1}$ which is close to the band corresponding to boroxol ring (806 cm$^{-1}$) indicates the predominance of boroxol rings in the structure of the glass. The somewhat strong and broad band around 442 cm$^{-1}$ indicates the presence of loose diborate and loose B0$_4$ groups. The broad band around 1305 cm$^{-1}$ may be assigned to delocalized B-O stretches occurring in large borate network. The shoulder around 770 cm$^{-1}$ and the band around 442 cm$^{-1}$ together with weak scattering around 650 and 950 cm$^{-1}$ may be considered as the proof of the presence of a small concentration of pentaborate groups in the glass structure. From the presence of bands around 795 and 1305 cm$^{-1}$ it may be inferred that the structure of the glass consists of continuous random network of boroxol rings[11,12].

For larger concentration of Fe$_2$O$_3$ the scattering was found to be very weak. In the spectrum in figure 5.9 the peak around 795 cm$^{-1}$ has almost disappeared and a new, very weak peak around 770 cm$^{-1}$ has appeared. Also there is a weak scattering around 450 cm$^{-1}$ indicating the presence of loose diborate and loose B0$_4$ groups. Even
though the scattering is poor for the entire range scanned, the peak showing the characteristic band of a continuous random network shows up clearly around 1421 cm\(^{-1}\).

(b) **Variation of concentration of CaO**

The effects of variation of concentration of CaO on the laser Raman spectra of CaO–B\(_2\)O\(_3\)–Al\(_2\)O\(_3\)–Fe\(_2\)O\(_3\) are shown in figure 5.10 and 5.11. For lower concentration (15 mol%) of CaO, the prominent bands are around 801 and 690 cm\(^{-1}\) (figure 5.10). In addition, there is a broad band around 1325 cm\(^{-1}\). The line around 801 cm\(^{-1}\) is very close to the band corresponding to the boroxol rings and hence this band indicates the presence of boroxol rings in the glass. The band around 690 cm\(^{-1}\) which is more intense than that around 801 cm\(^{-1}\) has to be assigned to either ring type metaborate (usually around 630 cm\(^{-1}\)) or chain type metaborate (usually around 730 cm\(^{-1}\)) which are observed in binary alkali borate glasses\([17]\). Since the simultaneous occurrence of bands around 930, 770, 650 and 500 cm\(^{-1}\) alone is a reliable indication of the presence of the pentaborate groups, the band around 690 cm\(^{-1}\) which is close to 650 cm\(^{-1}\) cannot be assigned to pentaborate groups. The broad band centred around 1325 cm\(^{-1}\) is assigned to the delocalized B–O stretching.
When the concentration of CaO is increased to 24 mol%, noticeable changes occur in the Raman spectra (figure 5.11). There is a band of appreciable intensity (though not the most prominent band) around 803 cm\(^{-1}\) indicating the presence of boroxol rings. There is no band around 700 cm\(^{-1}\) but there exists a band around 532 cm\(^{-1}\) which may be assigned to loose BO\(_4\) and loose diborate groups (metaborate groups are not present in this glass containing larger mol% of CaO). The band around 972 cm\(^{-1}\) may be considered to be close 1110 cm\(^{-1}\) indicating the presence of diborate groups. There is also a band around 1430 cm\(^{-1}\). From these observations it may be inferred that the variation of CaO does not affect the structure of this glass which consists of random network of boroxol rings.

(c) Variation of concentration of Al\(_2\)O\(_3\)

The effect of variation of Al\(_2\)O\(_3\) on the Raman spectra of CaO-B\(_2\)O\(_3\)-Al\(_2\)O\(_3\)-Fe\(_2\)O\(_3\) glasses for two different concentrations of Al\(_2\)O\(_3\) are shown in figure 5.12 and 5.13. The spectrum of the glass containing lower concentration (3 mol%) of Al\(_2\)O\(_3\) shows peaks around 775, 455 and 1321 cm\(^{-1}\). Also there is weak scattering around 950 and 650 cm\(^{-1}\). The absence of the 806 cm\(^{-1}\) is an indication of total conversion of boroxol rings into other groups. The peak around 775 cm\(^{-1}\) (which is close to 770 cm\(^{-1}\)), and
455 cm\(^{-1}\) together with weak scattering around 650 and 950 cm\(^{-1}\) may be attributed to pentaborate groups. The band around 455 cm\(^{-1}\) alone is an indication of the presence of loose \(\text{BO}_4\) and loose diborate groups. The prominent peaks around 1321 cm\(^{-1}\) is characteristic of a continuous random network.

The spectrum corresponding to the larger concentration of \(\text{Al}_2\text{O}_3\) (figure 5.13) is almost similar to that in figure 5.12 except that an additional weak peak appears around 1034 cm\(^{-1}\) which may be assigned to diborate groups\(^{[12]}\). The band around 777 cm\(^{-1}\) which is close to 770 cm\(^{-1}\) together with the band around 475 cm\(^{-1}\) and weak scattering around 680 cm\(^{-1}\) and 900 cm\(^{-1}\) may be considered as an indication of pentaborate groups. The 806 cm\(^{-1}\) peak is absent in figure 5.13 also showing the non-existence of boroxol rings. The peak around 475 cm\(^{-1}\) shows the presence of loose diborate and loose \(\text{BO}_4\) groups as in the case of glass containing lower concentration of \(\text{Al}_2\text{O}_3\). The evidence for the structure of the glass to be made up of a continuous random network is given by the existence of prominent band around 1332 cm\(^{-1}\). It has been reported in the case of ternary glasses containing \(\text{Al}_2\text{O}_3\) that addition of \(\text{Al}_2\text{O}_3\) to binary alkali borate glasses causes 806 cm\(^{-1}\) peak to recur. But in the present study it is seen that the 806 cm\(^{-1}\) peak corresponding to boroxol rings does
not appear even in the glass system of composition $20\text{CaO-66B}_2\text{O}_3-9\text{Al}_2\text{O}_3-5\text{Fe}_2\text{O}_3$.

(iv) General discussion

The laser Raman spectrum of cabal glass $20\text{CaO-65B}_2\text{O}_3-15\text{Al}_2\text{O}_3$, and the spectra of the quarternary glass systems $\text{Na}_2\text{O-CaO-B}_2\text{O}_3-\text{Al}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3-\text{CaO-B}_2\text{O}_3-\text{Al}_2\text{O}_3$ for different concentrations of the constituents have been recorded. The spectra have been discussed in the light of the Krogh-Moe hypothesis and in comparison with the spectra of reported binary and ternary glass systems. The structure of vitreous $\text{B}_2\text{O}_3$ is a continuous random network of boroxol rings. It is seen that in cabal glass consisting of $\text{CaO, B}_2\text{O}_3$ and $\text{Al}_2\text{O}_3$, the structure is mainly built up of random network of boroxol rings, but the addition of $\text{CaO}$ and $\text{Al}_2\text{O}_3$ to $\text{B}_2\text{O}_3$ has caused some percentage of boroxol rings transform mainly to pentaborate groups and to a fewer number of other groups like diborate groups, loose diborate and loose $\text{BO}_4$ groups.

The addition of a fourth oxide, $\text{Na}_2\text{O}$, is seen to affect the structure of the ternary cabal glass very much. Smaller concentration (15 mol%) of $\text{Na}_2\text{O}$ is found to cause a conversion of boroxol rings to pentaborate groups while a larger concentration (24 mol%) causes almost complete
conversion of the boroxol groups to pentaborate groups and a fewer number of other groups like diborate, loose diborate and loose $\text{BO}_4$ groups. The variation of concentration of $\text{CaO}$ in the quarter nary glass system $\text{Na}_2\text{O-CaO-B}_2\text{O}_3-\text{Al}_2\text{O}_3$ is found to have a profound influence on the structure of the glass. When the concentration of $\text{CaO}$ is small (5 mol%) the structure is found to be mainly built up of boroxol groups while at a larger concentration (15 mol%) boroxol groups have completely converted into pentaborate groups. The change in the concentration of $\text{Al}_2\text{O}_3$ in the glass is also found to influence the structure of the glass. At lower concentration of $\text{Al}_2\text{O}_3$ (5 mol%) the glass structure is found to consist of mainly pentaborate groups along with appreciable number of other groups. The scattering of this glass sample is found to be weak and not to indicate the predominance of a particular group. But at higher concentration (20 mol%) of $\text{Al}_2\text{O}_3$, the spectrum clearly indicates the large concentration of pentaborate groups in the structure of the glass.

The spectra of all the glass samples containing different concentrations of $\text{Na}_2\text{O}$, $\text{CaO}$ and $\text{Al}_2\text{O}_3$ exhibit clearly the band characteristic of a random network of the glass.
The addition of Fe$_2$O$_3$ as the fourth component to the ternary cabal glass CaO-B$_2$O$_3$-Al$_2$O$_3$ badly affects the quality of the Raman spectra. The scattering is very poor for all the samples analysed. At low concentration (2 mol%) of Fe$_2$O$_3$ the structure is found to be mainly built up of boroxol rings and a fewer number of pentaborate groups. But as the concentration of Fe$_2$O$_3$ is increased to 9 mol% the scattering is very poor and the features of the spectrum indicate that pentaborate groups are the main constituents of the glass structure. The variation of concentration of CaO is found not to have much effect on the structure; the indications from the spectra point to the predominance of boroxol rings along with fewer number of other groups. The variation of concentration of Al$_2$O$_3$ also does not affect the structure drastically but larger concentration of Al$_2$O$_3$ is found to improve the quality of the Raman spectrum. It is found that the structure of the glass is not altered by the variation in the concentration of Al$_2$O$_3$ and that the structure is mainly built-up of pentaborate groups along with a smaller number of diborate groups, loose diborate and loose BO$_4$ groups. The band characteristic of the random network of the glass is predominantly present in the spectra of all the glass samples analysed.
Figure 5.1  Laser Raman Spectrum of 20CaO-65B₂O₃-15Al₂O₃ glass

Figure 5.2  Laser Raman Spectrum of 10CaO-60B₂O₃-15Al₂O₃-15Na₂O glass
Figure 5.3  Laser Raman Spectrum of $10\text{CaO} - 5\text{B}_2\text{O}_3 - 15\text{Al}_2\text{O}_3 - 24\text{Na}_2\text{O}$ glass

Figure 5.4  Laser Raman Spectrum of $5\text{CaO} - 65\text{B}_2\text{O}_3 - 15\text{Al}_2\text{O}_3 - 15\text{Na}_2\text{O}$ glass
Figure 5.5  Laser Raman Spectrum of 15CaO-55B₂O₃-15Al₂O₃-15Na₂O glass

Figure 5.6  Laser Raman Spectrum of 10CaO-65B₂O₃-5Al₂O₃-20Na₂O glass
Figure 5.7 Laser Raman Spectrum of $10\text{CaO-50B}_2\text{O}_3-20\text{Al}_2\text{O}_3-20\text{Na}_2\text{O}$ glass

Figure 5.8 Laser Raman Spectrum of $20\text{CaO-68B}_2\text{O}_3-10\text{Al}_2\text{O}_3-2\text{Fe}_2\text{O}_3$ glass
Figure 5.9  Laser Raman Spectrum of $20\text{CaO} - 62\text{B}_2\text{O}_3 - 10\text{Al}_2\text{O}_3 - 8\text{Fe}_2\text{O}_3$ glass

Figure 5.10  Laser Raman Spectrum of $15\text{CaO} - 70\text{B}_2\text{O}_3 - 10\text{Al}_2\text{O}_3 - 5\text{Fe}_2\text{O}_3$ glass
Figure 5.11  Laser Raman Spectrum of 24CaO·61B₂O₃·10Al₂O₃·5Fe₂O₃ glass

Figure 5.12  Laser Raman Spectrum of 20CaO·72B₂O₃·3Al₂O₃·5Fe₂O₃ glass
Figure 5.13  Laser Raman Spectrum of 20CaO–66B₂O₃–9Al₂O₃–5Fe₂O₃ glass
5.6. Conclusion

The laser Raman spectrum of the ternary cabal glass CaO-B_2O_3-Al_2O_3 and the quarternary glass systems CaO-B_2O_3-Al_2O_3-Na_2O and CaO-B_2O_3-Al_2O_3-Fe_2O_3 have been recorded. The spectra have been discussed in the light of reported spectra of binary and ternary glasses. It is found that the addition of alkali and other oxides to B_2O_3 results in the transformation of boroxol groups, which are the basic structural units in vitreous B_2O_3, into polyborate groups. The Raman spectra of all the glass samples analysed in the present study indicate the random nature of the network of the glass. It is found that Raman spectroscopy can be effectively made use of in identifying the structural groups present in the glass.
Reference


