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Infrared spectroscopy of glasses and polycrystals in the series $x\text{Cs}_2\text{S} + (1 - x)\text{B}_2\text{S}_3$

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Abstract

The IR spectra of $x\text{Cs}_2\text{S} + (1 - x)\text{B}_2\text{S}_3$ glasses and polycrystals are reported for the first time. Glasses can be continuously formed by quenching between two stainless steel plates out to $x \sim 0.60$. Single-phase polycrystals appear to form at $x = 0.33, 0.50$, and 0.75 . The IR spectrum of $c\text{-Cs}_2\text{S}:2\text{B}_2\text{S}_3$ ($x = 0.33$) shows that this phase consists of the dithioborate group having equal numbers of three- and four-co-ordinated borons similar to that of $c\text{-Rb}_2\text{S}:2\text{B}_2\text{S}_3$. The Li, Na, and K dithioborate phases, however, consist solely of tetrahedral borons. The IR spectrum of $c\text{-Cs}_2\text{S}:\text{B}_2\text{S}_3$, the *meta*-thioborate phase ($x = 0.50$), shows that this phase consists of four-membered ring *meta*-thioborate groups, $\text{Cs}_2\text{B}_2\text{S}_4$, with two non-bridging and two bridging sulfurs. Contrasting this behavior, the IR spectra of $c\text{-M}_2\text{S}:\text{B}_2\text{S}_3$, with $\text{M} = \text{Na}, \text{K}$ and Rb , shows that these phases are solely comprised of six-membered ring *meta*-thioborate groups, $\text{M}_3\text{B}_3\text{S}_6$. For the polycrystal with $x = 0.75$, $c\text{-Cs}_3\text{BS}_3$, the IR spectrum indicates that this phase consists of trigonal *ortho*-thioborate groups, Cs_3BS_3 , similar to those of the Li, Na, K, and Rb phases. The IR spectra of glassy B_2S_3 has been shown by previous work to consist of equal fractions of isolated 'loose' trigonal groups and six-membered thioboroxyl ring groups. With the addition of Cs_2S to B_2S_3 in the low-alkali region ($x < 0.5$) and similar to the behavior of the Na, K, and Rb thioborate glasses, the absorption band of the tetrahedral borons at $\sim 600\text{--}750\text{ cm}^{-1}$ reaches a maximum in intensity at $x \sim 0.3$. Tetrahedral borons appear to form initially from the loose trigonal groups, similar in behavior to the other alkali thioborate glasses. The IR glasses in the high-alkali region, $x > 0.5$, resemble those of the other thioborate glasses where the fraction of the *meta*-thioborate groups decreases in preference to the formation of *ortho*-thioborate groups. Quite surprisingly, there is no IR spectral evidence of the formation of the four-membered ring Cs *meta*-thioborate groups in the glasses, even though this structure is observed in the polycrystals in this series. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, the structure and physical properties of alkali thioborate glasses $[1\text{--}26] x\text{M}_2\text{S} + (1 - x)\text{B}_2\text{S}_3$, where $\text{M} = \text{Li}, \text{Na}, \text{K}$ and Rb , have been studied in terms of their short range order (SRO) and intermediate range order (IRO) structures.

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Such structural information is important to the full understanding of the influence of structural changes on the bulk properties such as T_g , density, and the ionic conductivity of these glasses. In particular, the T_g measurements of the $M_2S + B_2S_3$ glasses [27] have shown that the T_g decreases ~ 150 °C with the addition of $x \sim 0.25$ M_2S and this contrasts similar measurements on the alkali borate glasses, where T_g increases ~ 300 °C with the addition of $x \sim 0.30$ M_2O [28–30]. This behavior indicates that the IRO structures and possibly the SRO structures in the alkali borate and thioborate glasses are quite different. Quite surprisingly, however, the density [7,11,31–33], the IR [2,4,5,15,31], and ^{11}B NMR [12,14,34–36] measurements all have shown that the SRO structures of the alkali thioborate glasses are very similar to those of the alkali borate glasses.

For example, the densities of the Na, K, Rb, and Cs glasses can be completely and accurately modeled using a SRO model that only includes four SRO structures, structures also found in the alkali borates, namely the trigonal boron with zero, one, and three non-bridging sulfurs, and the tetrahedrally coordinated boron. The composition dependence of the fractions of each group used to model the density was also found to follow trends very similar to those of the alkali borate glasses, excepting the tetrahedral boron group, as will be discussed below. Similarly the IR (excepting the Cs glasses) and NMR spectra of these alkali thioborate glasses can be wholly explained using only these four SRO structures and a composition dependence that is quite similar to that for the alkali oxide borate glasses.

In this paper, we report on our continued examination of the structures and properties of the alkali thioborate glasses by reporting recent IR studies of the $Cs_2S + B_2S_3$ glasses. Previous reports of the IR spectra of the other alkali thioborate glasses have been published.

2. Background

2.1. Structure and composition dependence of the short range order groups

B_2S_3 glass ($v\text{-}B_2S_3$) was found through multiple-quantum NMR measurements [17] to consist of

equal fractions of thioboroxyl ring groups, $B_3(S_3)S_{3/2}$, and trigonal groups, $BS_{3/2}$. This corresponds to a ratio of 3:1 for borons in ring groups to those in isolated trigonal groups. A similar ratio has also been recently reported by Zwanziger and co-workers [37,38] for B_2O_3 glass. Hence, the structures of B_2O_3 and B_2S_3 glass appear to be quite similar. This apparently simple result is actually quite surprising since the structure of $c\text{-}B_2S_3$ has been resolved [39,40] and is found to consist of equal numbers of four- and six-membered ring units. $c\text{-}B_2S_3$ does not contain loose trigonal units and our measurements of $v\text{-}B_2S_3$ shows that it does not contain four-membered ring units. With the addition of alkali sulfide to B_2S_3 , tetrahedral borons form at the expense of the trigonal groups with no non-bridging sulfurs, $B3(0)$. For the Na, K, and Rb thioborate glasses, the $B3(0)$ groups that are first consumed appear to be those in the isolated trigonal groups with the borons in the thioboroxyl rings unreacted until all the ‘loose’ triangle borons are consumed.

After the fraction of tetrahedral borons reaches a maximum concentration at $x \sim 0.3\text{--}0.35$, which, unlike the behavior in the alkali borate glasses, is a very strong function of the alkali, the trigonal group with one non-bridging sulfur, $B3(1)$, begins to form. These groups are organized into IRO structures of the *meta*-thioborate group, which are six-membered thioboroxyl rings with the ‘outside’ bridging sulfurs now terminated with alkali ions. The final SRO group to form in the alkali thioborate glasses is the fully depolymerized trigonal group $B(MS)_3$, $B3(3)$, where M is an alkali. It has been found that the structural groups intermediate between these, the pyro-thioborate group, $M_4B_2S_5$, $B3(2)$, apparently does not form in these alkali thioborate systems [10]. By this composition also, the glass forming character of the liquids has decreased significantly and only a few of the alkali thioborates can be readily quenched to glasses beyond $x \sim 0.65$. Fig. 1 shows the known and proposed SRO structures found in the alkali thioborate systems.

While the results above suggest that the SRO structures of the alkali thioborate glasses are quite similar to those found in the alkali borate glasses, other results show that the IRO structures must be

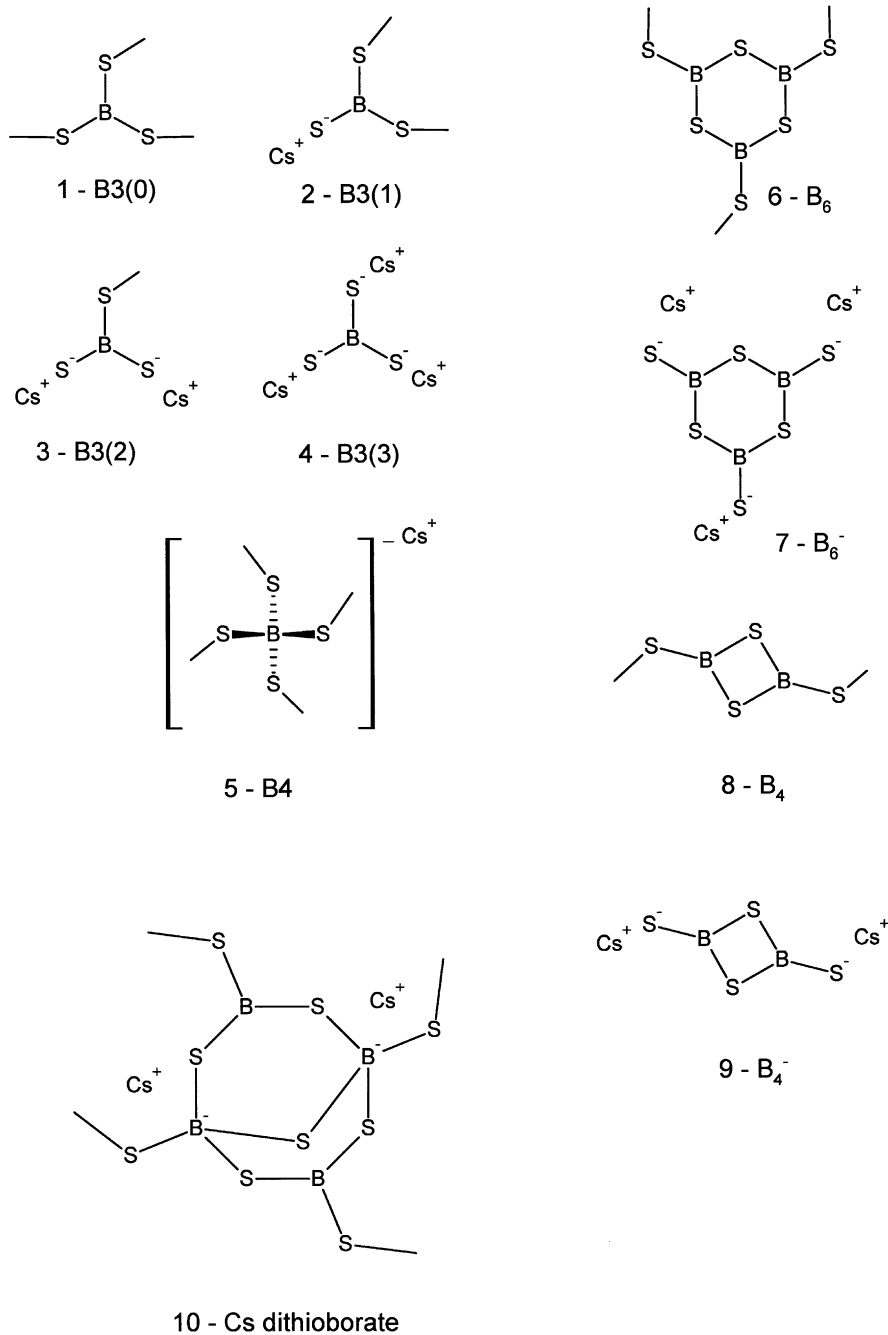


Fig. 1. SRO structures of the structural groups for alkali thioborate glasses.

significantly different as well. As noted above, the T_g s of the two series of glasses have opposite composition dependence in the low-alkali range; T_g

decreases with added M_2S to B_2S_3 , while T_g increases with added M_2O to B_2S_3 . One significant difference that has been correlated to differences in

the IRO between the two glasses is that the rate of formation of tetrahedral borons in the alkali thio-borate glasses depends strongly on the alkali. As found previously with ^{11}B NMR [41], the creation rate of tetrahedral borons is ~ 7 for the Na thio-borate glasses, ~ 3 for the K glasses, ~ 2.5 for the Rb glasses, and 2 for the Cs glasses. The Na glasses have so far been the most thoroughly examined and the finding appears to be that the Na glasses form molecular anions of the type found for other thio-borate phases. Most notably, at $x\text{Na}_2\text{S} = 0.375$, a phase appears to form that consists of molecular anions of formula $\text{Na}_6\text{B}_{10}\text{S}_{18}$, where all B atoms are found to be four co-ordinated [42]. Such units, while giving rise to the high fractions of tetrahedral borons, would not be expected to create a more highly polymerized melt. Rather, their formation would be expected to depolymerize the melt and hence lower T_g with added Na_2S as seen experimentally.

Other more detailed studies such as Raman and high resolution NMR of the other alkali thio-borate glasses are in progress to examine the IRO in these glasses and will be reported in future publications.

2.2. IR spectra of the alkali thio-borate phases

The IR spectra of the alkali (Li, Na, K, and Rb) thio-borate glasses and polycrystals [2,4,5,15,31] have shown that the local SRO structure of these glasses is dependent on the nature of the alkali ion present. It has been proposed that the structure of the Li, Na and K dithio-borate polycrystals, $\text{M}_2\text{S}:2\text{B}_2\text{S}_3$, are iso-structural, where all of the borons are in tetrahedral co-ordination. A tentative structure has been suggested [41]. However, the structure of the Rb dithio-borate polycrystal shows evidence that this phase consists of both trigonal and tetrahedral borons in approximately equal amounts and as such it has been suggested that the Rb dithio-borate phase is iso-structural with the alkali diborate phase.

Interestingly, the IR spectra of the Li *meta*-thio-borate phase, $c\text{-Li}_2\text{S}:\text{B}_2\text{S}_3$ [5], shows that it is comprised of all four-co-ordinated borons. In contrast to this behavior, the IR spectra of $c\text{-M}_2\text{S}:\text{B}_2\text{S}_3$ (M = Na, K and Rb) phases show that they are comprised of six-membered ring *meta*-thio-borate units ($\text{M}_3\text{B}_3\text{S}_6$). The IR spectra of the alkali *ortho*-thio-borate phases, $c\text{-M}_3\text{BS}_3$, are strikingly similar and all consist of isolated M_3BS_3 groups. The vibrational frequency of the band decreases slightly with the heavier alkali ions, as would be expected.

The lithium thio-borate glasses can only be prepared above $x = 0.5$ due to liquid–liquid phase separation in the low-alkali region. As such, glasses begin with a high fraction of tetrahedral borons that are steadily converted to isolated *ortho*-thio-borate groups at the end of the glass forming range at $x\text{Li}_2\text{S} = 0.75$.

The IR spectra of the Na, K, and Rb thio-borate glasses [2,4,43] indicate that the monotonic increasing fraction of BS_4 groups is accompanied by the destruction of trigonal borons in the low-alkali region. In the high-alkali region, the increase in the fraction of *ortho*-thio-borate groups through the consumption of tetrahedral borons and *meta*-thio-borate groups is the main structural change. However, the structure of the Rb thio-borate glasses [2] in the high-alkali region appears to consist of the *meta*-thio-borate groups, *ortho*-thio-borate groups, and tetrahedral boron groups. Unlike the alkali borate glasses, the structure of the alkali thio-borate glasses and polycrystalline compounds are strongly influenced by the modifier cation.

In this study, the IR spectra of $x\text{Cs}_2\text{S} + (1 - x)\text{B}_2\text{S}_3$ glasses and polycrystals in the $0 \leq x \leq 0.65$ range are reported for the first time to extend the study of the alkali thio-borate series.

3. Experimental methods

High purity Cs_2S powders were prepared from direct reaction of Cs metal (99.9%, ESPI) and crystalline sulfur (99.999%, Cerac) at 300 °C in a bare quartz tube for two days. To prepare $v\text{-B}_2\text{S}_3$, amorphous boron (99.99%, Cerac) and crystalline sulfur (99.999%) were reacted in a rotated (~ 5 rpm) carbon-coated quartz tube at 850 °C for 7 h.

$x\text{Cs}_2\text{S} + (1-x)\text{B}_2\text{S}_3$ glasses were prepared by mixing stoichiometric amounts of B_2S_3 and Cs_2S and melted in a covered vitreous carbon crucible with a lid for ~ 5 min at ~ 650 – 750 °C using a muffle furnace (Thermolyne) inside the glove box (< 10 ppm H_2O and O_2). For the IR spectra, thin glass films were blown in the composition range 0–35 mol% Cs_2S . For the composition range, $0.4 \leq x \leq 0.6$, the melts were quenched into stainless steel molds. The polycrystals for $x = 0.33, 0.5$ and 0.75 were prepared in vacuum-sealed, carbon-coated quartz tube using solid-state reaction of $v\text{-B}_2\text{S}_3$ and Cs_2S at ~ 400 – 500 °C for 10 days.

IR spectra were taken on an FT-IR spectrometer (Bio-Rad FTS-40) using KBr pellets of the polycrystals or the thin films of the glasses sandwiched between two single crystal KBr pellets separated by a gas-tight rubber o-ring. For polycrystals and glasses in the high-alkali region, samples for the IR spectra were made by diluting the glass 1:10 in dried IR-grade KBr and mixing in an agate mortar and pestle and pressed into pellets.

4. Results

4.1. IR spectra of the polycrystals

As seen in Fig. 2, the IR spectra for $c\text{-M}_2\text{S}:2\text{B}_2\text{S}_3$ ($M = \text{Li}, \text{Na}, \text{K}$) polycrystalline phases show two sets of strong doublets centered at ~ 650 and ~ 750 cm^{-1} . These modes have been previously assigned to vibrations of the tetrahedral boron group and these assignments are shown in Table 1. The strong similarity of the absorption bands indicates a strong structural similarity as well. The lack of any significant absorption intensity above 750 cm^{-1} suggests that these phases are comprised solely of tetrahedral boron groups. This hypothesis is supported by ^{11}B NMR measurements that show that there are only tetrahedral borons in these phases.

The IR spectrum of the Rb dithioborate polycrystal also shows these two doublets, although not as well resolved, but this phase also shows additional absorption bands at ~ 800 cm^{-1} (weak) and ~ 925 cm^{-1} (strong). Hence, while this phase

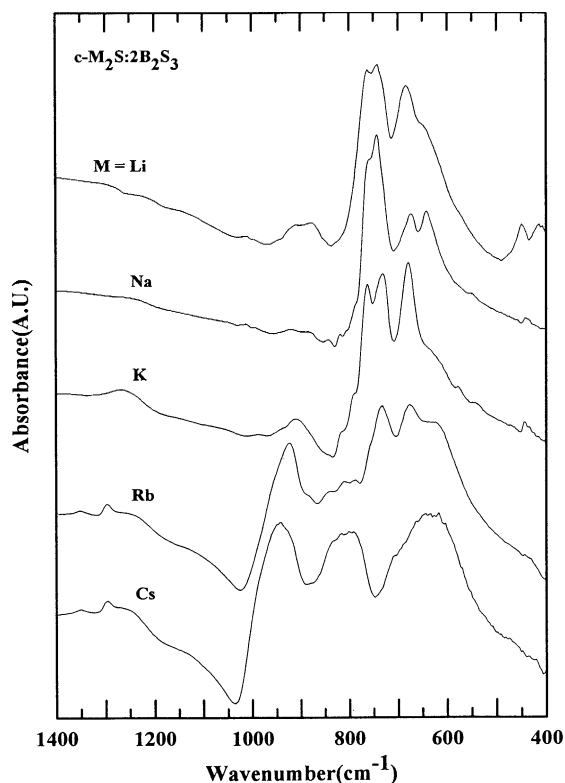


Fig. 2. IR spectra of KBr pellets of $c\text{-M}_2\text{B}_4\text{S}_7$ ($\text{Na}, \text{K}, \text{Rb},$ and Cs).

does contain tetrahedral borons, it must also contain trigonal boron groups as well. From the spectra of the *meta*-thioborate groups shown below, the mode at ~ 925 cm^{-1} is associated with six-membered ring groups. The IR spectrum of the Cs dithioborate phase shows absorption in three spectra regions; a strong mode centered at 650 cm^{-1} , a mode centered at ~ 800 cm^{-1} , and a mode centered at ~ 950 cm^{-1} . The presence of these three modes suggest that the Cs dithioborate phase consists of tetrahedral boron groups, isolated trigonal groups, and six-membered ring groups.

In addition, the absorption band mode at ~ 650 cm^{-1} is a weak broad singlet for the Cs phase. While such behavior is not fully understood, it is likely associated with the fact that a smaller conversion rate from trigonal borons to tetrahedral borons is observed as the size of the alkali ion increases. Namely, the conversion rate from tri-

Table 1
Symmetry analysis for SRO and IRO groups proposed for alkali thioborate glasses

Structural type	Vibrational modes	Activity
B3(O) and B3(3)	A'_1	Raman
	$2E'$	IR, Raman
	A''_2	IR
B4	A_1	Raman
	$2T_2$	IR, Raman
	E	Raman
Four-membered ring	$3A_{1g}$	Raman
	$2B_{1g}$	Raman
	B_{2g}	Raman
	$2B_{1u}$	IR
	$2B_{2u}$	IR
	$2B_{3u}$	IR
Six-membered ring	$3A'_1$	Raman
	$2A'_2$	Inactive
	$5E'$	IR, Raman
	$2A''_2$	IR
	$2E''$	Raman

gonal borons to tetrahedral borons is ~ 6 – 8 and ~ 3 per added sulfide ion for the Na and K thioborate glasses [34], respectively, whereas the conversion rate is ~ 2.5 and 2 for the Rb and Cs thioborate glasses, respectively. The higher frequency modes are associated with trigonal boron units and as such would be expected to be more prevalent the smaller the fraction of tetrahedral borons (for example, $c\text{-Na}_2\text{S:}2\text{B}_2\text{S}_3$ is known to have $N_4 = 1$ and no modes above $\sim 800\text{ cm}^{-1}$ are seen in the spectra).

We have already reported that the bands between ~ 600 and 750 cm^{-1} arise from tetrahedral borons and the modes at ~ 800 and $\sim 950\text{ cm}^{-1}$ arise from isolated *ortho*-thioborate trigonal groups and *meta*-thioborate six-membered ring groups, respectively [1]. In a manner similar to the structure of the Rb dithioborate phase, the Cs phase may exhibit a diborate-like structure in which it is comprised equal fractions of tetrahedral and trigonal borons (see Fig. 1).

As seen in Fig. 3, the IR spectra of $c\text{-M}_2\text{S:B}_2\text{S}_3$ (alkali *meta*-thioborate) ($M = \text{Na}, \text{K}, \text{and Rb}$) phases are quite different from that of the Cs phase. The IR spectra of the Na, K and Rb phases show an intense band envelope centered at ~ 900

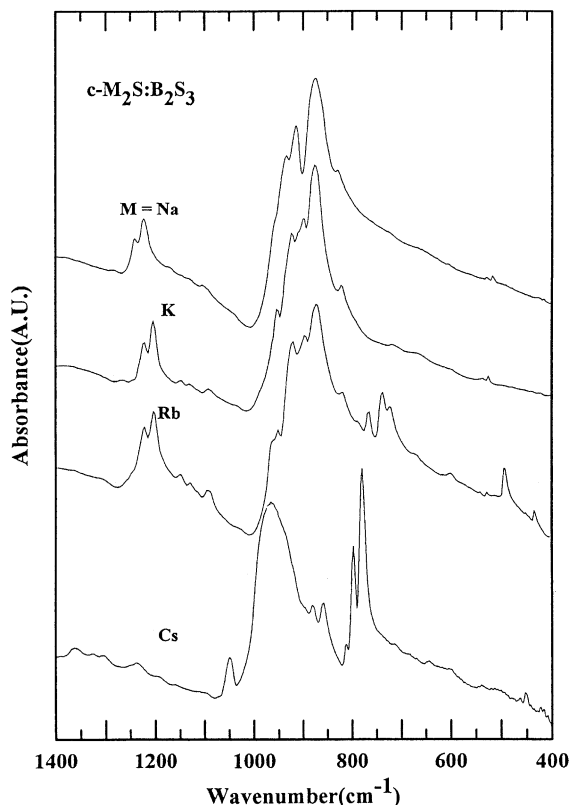


Fig. 3. IR spectra of KBr pellets of $c\text{-MBS}_2$ ($M = \text{Na}, \text{K}, \text{Rb}, \text{and Cs}$).

cm^{-1} which is attributed to the *meta*-thioborate six-membered ring vibrations. However, the IR spectrum of the Cs *meta*-thioborate polycrystal shows two band envelopes, one at $\sim 1000\text{ cm}^{-1}$ and one at $\sim 800\text{ cm}^{-1}$. The SRO structure of $c\text{-Cs}_2\text{S:B}_2\text{S}_3$ has been resolved and has been shown to consist of four-membered ring groups with two non-bridging and two bridging sulfurs and of formula $\text{Cs}_2\text{B}_2\text{S}_4$ [44]. This structural unit is shown in Fig. 1. The band at $\sim 800\text{ cm}^{-1}$ is therefore assigned to the vibration of BS_3 groups in the four-membered rings and the band at $\sim 950\text{ cm}^{-1}$ to the vibration of the four-membered ring groups. This is the only structure so far resolved that is found to possess these four-membered rings besides $c\text{-B}_2\text{S}_3$. The crystal structure of B_2S_3 is comprised of equal amounts of six- and four-membered rings groups. So far, however, no evidence of four-membered rings has been found for the other alkali

thioborate glasses. It is a key part of this study to determine whether these four-membered rings found in both $c\text{-B}_2\text{S}_3$ and in $c\text{-Cs}_2\text{B}_2\text{S}_4$ are also found in the Cs thioborate glasses.

Fig. 4 shows that at $x = 0.75$ the IR spectrum of $c\text{-}3\text{Cs}_2\text{S}:\text{B}_2\text{S}_3$ is similar to those of $c\text{-}3\text{M}_2\text{S}:\text{B}_2\text{S}_3$ ($\text{M} = \text{Li}, \text{Na}, \text{K}$ and Rb) and the strong band at $\sim 800\text{ cm}^{-1}$ is assigned to the vibration of the isolated *ortho*-thioborate ($\text{B}3(3)$) group. The peak frequency of the mode for each phase shifts to lower frequencies as would be expected from the increasing mass of the alkali counter-ion in these phases. These absorption bands are also found to be multiplets and as will be shown below in the vibrational analysis of these groups this arises from two sets of modes closely spaced in frequency.

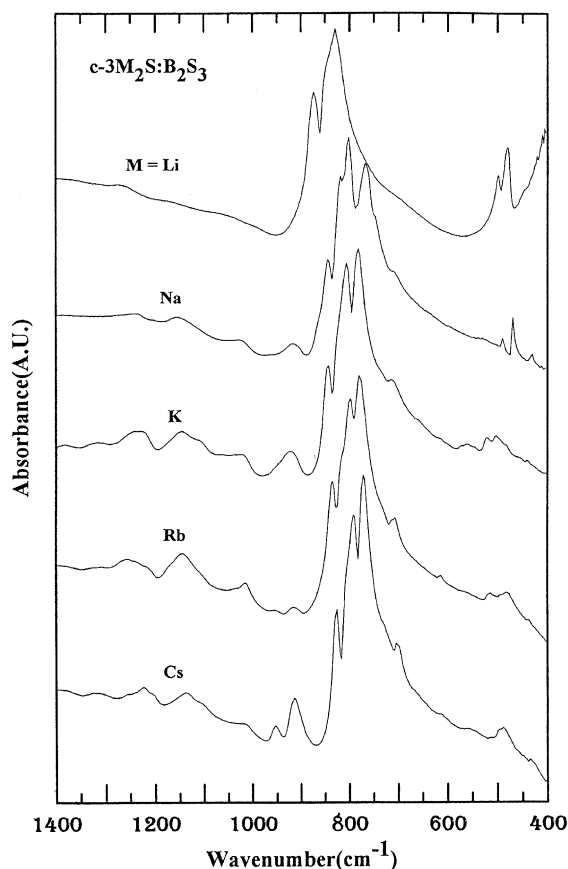


Fig. 4. IR spectra of KBr pellets of $c\text{-M}_3\text{BS}_3$ ($\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb},$ and Cs).

4.2. IR spectra of glasses

4.2.1. Low-alkali glasses ($x < 0.35$)

The IR spectra of the low-alkali ($x < 0.35$) Cs thioborate glasses are shown in Fig. 5. The very weak absorption bands above 1200 cm^{-1} are associated with a minor amount ($<1\%$) of oxide contamination that is always present in these glasses. While high purity starting materials are used and careful preparation techniques are employed, no extreme precautions such as subliming or distilling of the starting materials is performed. Such high purity precautions are routinely performed for chalcogenide glasses used in IR optical fiber applications where very low oxygen levels are required to enable high transmission in the IR region. Such purity levels are not required here since they will not alter the bulk structure of the glasses significantly.

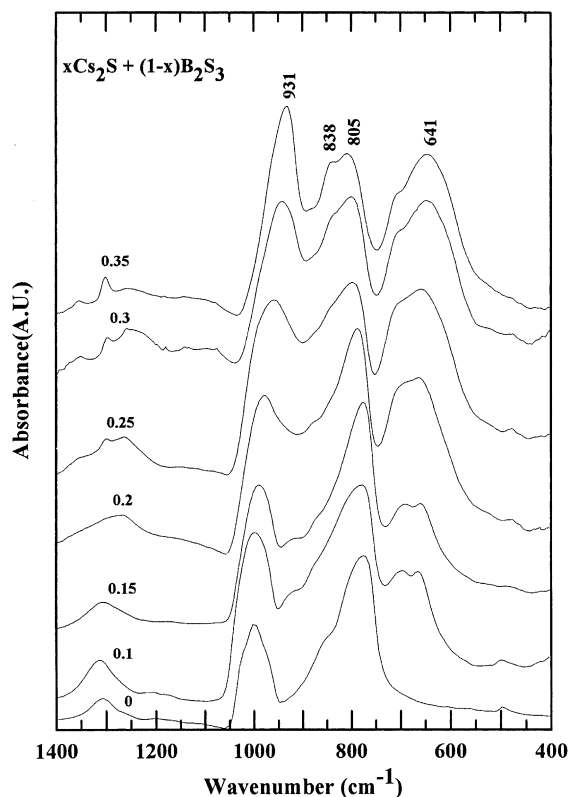


Fig. 5. IR spectra of thin film glasses of $x\text{Cs}_2\text{S} + (1-x)\text{B}_2\text{S}_3$, $0 \leq x \leq 0.35$.

The IR spectrum of B_2S_3 glass consists of two strong absorption bands centered at ~ 1000 and ~ 800 cm^{-1} , respectively. These bands have been previously ascribed to the vibrations of six-membered ring and loose trigonal groups, respectively [10,43]. As Cs_2S is added to B_2S_3 , a new mode develops at ~ 650 cm^{-1} and as described above this mode is assigned to the formation of tetrahedral borons in the glass. The relative intensity of the 1000 and 800 cm^{-1} modes changes with x where by $x = 0.35$, the mode at 1000 cm^{-1} , now shifted to ~ 930 cm^{-1} , has become the dominate mode. This suggests that the borons giving rise to the 800 cm^{-1} mode are the same borons responsible for the formation of the tetrahedral borons. Hence, it is likely that the tetrahedral borons are formed from the loose trigonal groups rather than the six-membered ring groups. Such behavior has been observed for the other alkali thioborate glasses.

It is also in this same compositional region that the six-membered ring group changes over from being a neutral covalent structure in B_2S_3 glass to an ionic structure comprising of three ionic M–S bonds on the *meta*-thioborate group, see Fig. 1. This is accompanied by the small, but important, frequency shift, from ~ 1000 to ~ 930 cm^{-1} . What is particularly striking about these Cs thioborate glasses is the observation that $c\text{-}Cs_2B_2S_4$ exhibits a strong absorption band at ~ 970 cm^{-1} and as such it would be expected that the glasses would exhibit a similar band in this frequency range as this group is formed in the glasses. While the frequency difference between 930 and 970 cm^{-1} is not large, it is beyond the experimental error and, therefore, it is believed that for some as yet unknown reason, the four-membered ring group does not form in these glasses. Rather, it is believed that the *meta*-thioborate group to form in these glasses is that of the six-membered ring structure. Such differences between the structure of the glasses and polycrystals are not observed in the other alkali thioborate systems.

4.2.2. High-alkali glasses ($x > 0.35$)

Fig. 6 shows the IR spectra of the glasses with $xCs_2S > 0.35$. Here the oxide contamination of the glasses appears to be slightly higher than that seen for the low-alkali glasses and likely suggests that

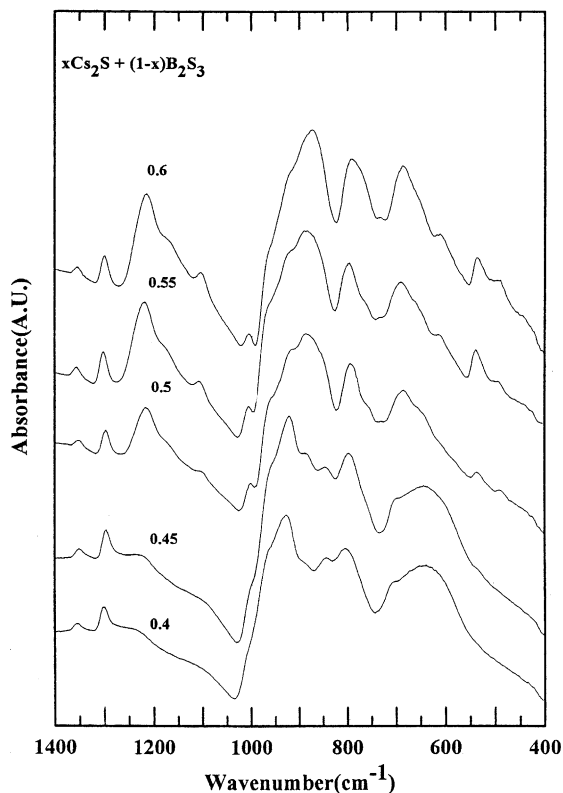


Fig. 6. IR spectra of KBr pellets of glasses of $xCs_2S + (1-x)B_2S_3$, $0.4 \leq x \leq 0.6$.

the source of the oxide contamination is the Cs_2S , known to be a very reactive material. The spectra show less compositional dependence when compared to the low-alkali glasses and while this is associated with a smaller compositional range, it is also associated with the fact that less structural change is occurring in this compositional range.

The mode at ~ 950 cm^{-1} associated with the six-membered ring group significantly broadens and becomes more intense, while the opposite is true of the mode at ~ 650 cm^{-1} , associated with the tetrahedral boron group. This likely is the result of the fact that the six-membered ring group becomes the dominant structural group in the vicinity of $x = 0.5$, whereas the tetrahedral boron group is becoming the least prominent structural group in the glass.

Similarly, the mode centered at ~ 800 cm^{-1} and assigned to the loose trigonal boron group,

gradually becomes broader and more intense. While it does not become the dominant mode at the end of the glass forming range of this series of glasses, this is to be expected since it would be the dominant structure only at $x = 0.75$. That glasses cannot be formed beyond $x = 0.6$ terminates the formation of this group before it can become the dominant structural group. In the other series of glasses, Li, Na, and K, in particular, that can be formed out to $x = 0.75$, the IR spectra clearly show that this structural group becomes the dominant group in the glass at this composition [4,5,43].

Significantly though, the Rb glasses behave quite differently and even though they can be formed out to $x = 0.75$, where the dominant structural group should be the *ortho*-thioborate phase, the glass at $x = 0.75$ exhibits bands associated with the three structural groups, the tetrahedral boron group, the *meta*-thioborate group, and the *ortho*-thioborate group. This behavior to be more completely discussed below, is thought to be associated with the disproportionation of the structures into the lower alkali structures with a concomitant generation of free Rb_2S in the melt. The possibility of the same behavior here accounting for the apparent high fraction of *meta*-thioborate and tetrahedral boron groups in the glass cannot be ignored.

5. Discussion

5.1. Vibrational analysis of the structural groups

As a first step in analyzing the IR spectra of the glasses and polycrystals in this series, the vibrational symmetry analysis of the various SRO groups expected to be found in this series are reviewed. Table 1 gives the SRO structure, the point group of the structure, and the activity of the mode. As can be seen from Table 1, there are many modes which are both IR and Raman active as well as modes that are only IR or Raman active. This difference in activity was used as a powerful tool in interpreting the IR and Raman spectra of the Na thioborate glasses. The Raman spectra of the other heavier alkali thioborate glass series have

not been performed yet, but will be the subject of future publications. The purpose here is to recognize that symmetry analysis will provide significant guidance in analyzing the IR spectra of these glasses and polycrystals.

5.2. Interpretation of the IR spectra of the polycrystals

We have reported the IR spectrum of $\text{c-B}_2\text{S}_3$ previously, but unfortunately, due to the great difficulty in obtaining this crystalline form (B_2S_3 is an extremely strong glass former), the material was only partially crystallized [10,43]. However still, the IR spectra shows two main absorption envelopes, one centered at $\sim 1000\text{ cm}^{-1}$ and one centered at $\sim 800\text{ cm}^{-1}$. The mode at 800 cm^{-1} has been previously assigned to the A'_2 and E' modes of the loose $\text{B}_3(0)$ triangle units. The higher frequency 1000 cm^{-1} mode has been assigned to the 'breathing' E' modes of the six-membered rings units. It was not clear from our original IR spectra of this compound whether or not this band envelope also contains the B_u modes of the four-membered ring. However, now with access to the phase $\text{c-Cs}_2\text{B}_2\text{S}_4$, that is known to contain only four-membered rings, the IR spectrum of which is shown in Fig. 3 above, it is possible to make the determination of whether the IR spectra indicates that $\nu\text{-B}_2\text{S}_3$ contains four-membered units or not ($\text{c-B}_2\text{S}_3$ is known to contain equal numbers of four and six-membered rings).

The IR spectrum of $\text{c-Cs}_2\text{B}_2\text{S}_4$ shows a strong absorption band at $\sim 964\text{ cm}^{-1}$, in the vicinity of the 1000 cm^{-1} mode for both the partially crystalline and glassy B_2S_3 . The IR spectra of $\text{c-Na}_3\text{B}_3\text{S}_6$, known to be comprised solely six-membered rings [45], also shows a strong absorption band centered at $\sim 900\text{ cm}^{-1}$. Hence, the high frequency mode in the IR spectra of $\nu\text{-B}_2\text{S}_3$ could be considered consistent with arising from either six- or four-membered rings. Recent neutron scattering results for $\nu\text{-B}_2\text{S}_3$ show definitively [46], however, that there are no four-membered rings in this glass and as a result, we must conclude here that the high frequency mode for $\nu\text{-B}_2\text{S}_3$ arises from the six-membered ring units in the glass and not from four-membered rings.

The significant difference in the IR spectra of the different alkali diborate polycrystals is that the heavier alkali dithioborate phases show the presence of both six-membered rings units (Rb), absorption at $\sim 950\text{ cm}^{-1}$, and trigonal units (Cs), absorption at $\sim 800\text{ cm}^{-1}$, compared to the lighter alkali that only show absorption below 800 cm^{-1} . The Li, Na, and K dithioborate polycrystals show evidence for only tetrahedral boron units. These assignments have recently been corroborated by ^{11}B NMR measurements on these phases, where the Na and K dithioborate phases were found to be comprised solely of tetrahedral borons and both the Rb and Cs dithioborate crystalline phases were found to have equal fractions on trigonal and tetrahedral boron groups. Such an assignment is supported by similar measurements of the tetrahedral boron fraction in the glasses, where it was found that Rb and Cs thioborate glasses behave according to the $N_4 \sim x/1-x$ rule where two tetrahedral borons are formed for every formula unit of M_2S added to the glasses. Such a formation rate of tetrahedral borons would necessarily produce an N_4 of 0.5 at $x = 0.33$. It is likely, therefore, that the dithioborate phase of Rb and Cs exhibit a structure similar to the alkali diborate where half of the borons are in trigonal and half are in tetrahedral co-ordination. A plausible structural model is shown in Fig. 1.

One of the surprising results found for the $\text{Cs}_2\text{S} + \text{B}_2\text{S}_3$ system is that the structure of the Cs *meta*-thioborate structure is not congruent with the other alkali *meta*-thioborates of Na, K, and Rb. Rather than possessing the six-membered thioboroxyl ring structure like the other alkali thioborates, the $\text{c-Cs}_2\text{S}:\text{B}_2\text{S}_3$ exhibits the four-member ring structure, as shown in Fig. 1. The four-membered ring structure is also observed in $\text{c-B}_2\text{S}_3$ as discussed above, but also surprisingly is not observed in the $\nu\text{-B}_2\text{S}_3$. The vibrational symmetry analysis of the four-membered ring structure is presented in Table 1 and the comparison of the IR and Raman spectra is shown in Fig. 7. As expected from the symmetry analysis, the IR and Raman spectra do not share any similar modes. The somewhat expected and yet disappointing result is that the IR absorption frequency of this structure, as described above, lies very close to the frequency

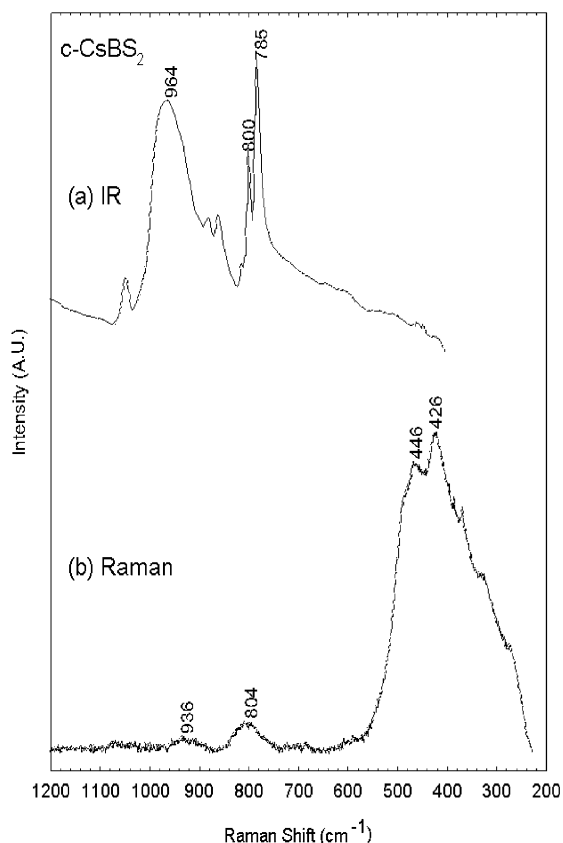


Fig. 7. Comparison of the IR spectra and Raman spectra of c-CsBS_2 . Taken with permission from Ref. [42].

range of the six-membered thioboroxyl ring mode. This will make determining whether the Cs thioborate glasses contain these four-membered rings more complicated. So far it has been determined that $\nu\text{-B}_2\text{S}_3$ does not contain them and a critical question is whether as the fraction of Cs_2S approaches whether the four-membered ring begins to form near the stoichiometric fraction of $x = 0.5$, as is expected from the behavior of the other alkali thioborate glasses.

There is some evidence that not all SROs expected from composition and the crystal structures form in the corresponding glasses. For example, in the Na, and Rb glasses, it appears that the 2:1 phase, the pyro-thioborate phase, B3(2), does not form, but rather the SRO converts directly from the *meta*-thioborate phase, B3(1), to the

ortho-thioborate phase, B3(3) [10]. We will explore the question of whether the four-membered ring forms in these glasses in some detail below.

The final SRO structure to be assigned is the B3(3) group, the *ortho*-thioborate group. As seen in Fig. 3 above, there is a single absorption multiplet centered about $\sim 770\text{ cm}^{-1}$. This mode from the symmetry analysis in Table 1 likely is comprised of the E' modes, the doublet centered at $\sim 800\text{ cm}^{-1}$, and the A'_2 mode centered at 770 cm^{-1} . The A'_2 mode is assigned to the lower frequencies since it is a bending mode compared to the stretching E' mode. It is significant to note that the frequency of this mode is relatively unchanged from the frequency of the neutral B3(0) trigonal group, 772 cm^{-1} in $v\text{-B}_2\text{S}_3$ compared to the identical frequency of $\sim 770\text{ cm}^{-1}$ for the $c\text{-Cs}_3\text{BS}_3$ phase. This suggests that this mode is only weakly coupled to the bridging sulfurs in $v\text{-B}_2\text{S}_3$ for the former and to the charge compensating Cs^+ cations for the latter. Similar results were found for the other alkali *ortho*-thioborate phases.

5.3. Interpretation of the IR spectra of the glasses

5.3.1. Low-alkali glasses ($x < 0.4$)

The dominant change in the IR spectra of the low-alkali glasses, $x \leq 0.35$ is the development of the new absorption band centered at $\sim 650\text{ cm}^{-1}$ and the growth in its intensity with added Cs_2S . As described above, this band is attributed to the formation of tetrahedral borons being formed at the stoichiometric rate of two tetrahedral borons for every added Cs_2S following the $N_4 = f_{\text{B}_4} = x/1 - x$ rule [29]. This band appears to be a doublet and this is as predicted by the symmetry analysis of the tetrahedral unit. The relative integrated intensity of this mode is plotted in Fig. 8 as is the ^{11}B NMR measured N_4 data and the agreement is quite good, again lending support to the assignment of this band to vibrations of the tetrahedral boron unit. The frequency of this band is very similar to that observed for the same band in the other alkali thioborate glasses, especially to that of Rb thioborate glasses, cf. 640 versus 641 cm^{-1} . The lighter alkali also exhibit a frequency of $\sim 650\text{ cm}^{-1}$ for this band as well, with the Li and

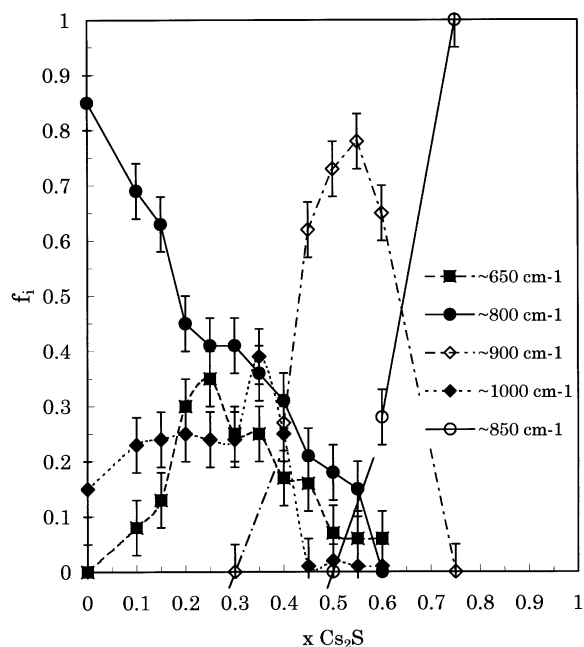


Fig. 8. Composition dependence of the relative area five main absorption peaks observed for $x\text{Cs}_2\text{S} + (1-x)\text{B}_2\text{S}_3$ glasses. Relative areas determined by deconvoluting of the IR spectra shown in Figs. 5 and 6 and described in the text.

Na glasses as expected from their lighter mass exhibiting and higher frequency of $\sim 700\text{ cm}^{-1}$.

As described above, the spectra of $v\text{-B}_2\text{S}_3$ has been previously interpreted as arising from the breathing mode of the six-membered ring unit at $\sim 1000\text{ cm}^{-1}$ and the stretching vibration of the isolated trigonal group at $\sim 770\text{ cm}^{-1}$. The band for the six-membered ring mode at $\sim 1000\text{ cm}^{-1}$ is a set of five E' modes and the band at 770 cm^{-1} is comprised of two separate modes. The A'_2 mode is assigned to the high frequency shoulder at $\sim 850\text{ cm}^{-1}$ and the two E' modes are assigned to the more intense main peak centered at $\sim 770\text{ cm}^{-1}$. As Cs_2S is added to $v\text{-B}_2\text{S}_3$, the frequencies of these two bands remains unchanged up to $x \sim 0.2$. However, the relative integrated intensity of the six-membered ring mode increases compared to that of the bands arising from the trigonal groups, and as described above, this suggests that the trigonal groups are the source of the borons being converted to tetrahedral co-ordination. Above $x \sim 0.2$, all of the loose trigonal groups would be

expected to be consumed (at a rate of $x/(1-x)$) and as such the six-membered rings would need to be converted to tetrahedral borons to accommodate a still increasing tetrahedral boron fraction. The frequency shift of the six-membered ring mode from ~ 1000 to ~ 930 cm^{-1} , as seen in Fig. 5, suggests that structural modification of this unit is taking place. Not only are these units being converted to tetrahedral borons, thereby reducing their concentration, but they are also being converted to *meta*-thioboroxyl rings units. This explains why the relative intensity of the band remains high even though a fraction of them are being converted to tetrahedral borons.

Similarly, the band arising from the trigonal units undergoes a frequency shift in this same compositional range. The mode shifts from being centered at ~ 770 cm^{-1} for $\nu\text{-B}_2\text{S}_3$ to being centered at ~ 820 cm^{-1} for $x = 0.35$. This apparently is associated with the change of the structural unit from being an isolated unit to that contained in the six-membered ring unit. In the section below, it will be seen that this mode shifts back again to lower frequencies as it is ‘released’ from the six-membered rings into forming isolated *ortho*-thioborate trigonal groups.

Finally, it is significant to note that at the dithioborate composition, $x = 0.33$, the IR spectra of the glass is comprised of six-membered ring units, trigonal units, and tetrahedral boron units. As described above for the polycrystals of this composition, this suggests that the structure of the glass may well be similar to that of the diborate phase for the oxide system, where half of the borons are in trigonal and half are in tetrahedral coordination. This is consistent with the measured N_4 values for these glasses and contrasts the behavior for the lighter alkali thioborate glasses, especially the Na thioborate glasses, where the exceptionally high tetrahedral boron fraction consumes nearly all of the trigonal borons in the glass.

5.3.2. High-alkali glasses ($x > 0.4$)

The spectra of the high-alkali glasses, $x \geq 0.50$, are shown in Fig. 6. The spectra are somewhat noisier than those of the low-alkali glasses because due to the rapidly decreasing glass forming

ability of the high-alkali glasses, thin films could not be blown on of these glasses. Rather, KBr pellets of these compositions were made and the IR spectra then collected. There is slight interaction between the KBr and the glass matrix and as such the band shapes become moderately distorted.

The significant feature for these spectra is that the spectra are only slightly different; there is not the major spectral change as is seen in the spectra for the low-alkali glasses. Nevertheless, the mode assigned to the now forming *meta*-thioborate group broadens significantly at $x = 0.5$ and decreases in frequency from ~ 930 to ~ 870 cm^{-1} . This frequency shift suggests the full formation of the *meta*-thioborate ring structure as evidenced by the frequency shifts of the *meta*-thioborate structures shown in Fig. 3. The Rb *meta*-thioborate ring group has an absorption band centered at ~ 900 cm^{-1} and the heavier mass of the Cs^+ ion would suggest that the Cs *meta*-thioborate ring vibration would lie below 900 cm^{-1} and the observed frequency of ~ 870 cm^{-1} is consistent with this behavior.

What is striking about this assignment though is the fact that the Cs *meta*-thioborate polycrystal structure is not comprised of six-membered rings, but rather as described above, is comprised of four-membered rings. Fig. 3 above shows that this unit has an absorption band frequency centered at ~ 950 cm^{-1} , far above and well separated from the observed ~ 870 cm^{-1} for the Cs thioborate glasses. This frequency difference strongly suggests that not only does the four-membered ring not form in $\nu\text{-B}_2\text{S}_3$, but it also does not form in the Cs thioborate glasses as well. The reasons for this behavior may have to do with the constrained bonding of the four-membered ring, where the crystal structure by Krebs suggests that the S–B–S bond angle is on the order of 90° , far smaller than the expected tetrahedral angle of 109° . Perhaps the glass structure allows this angle to relax and in so doing allows the structure to form trigonal units, both loose and those contained in six-membered rings. Further study of these phases by Raman and NMR spectra is being conducted to examine the formation of four-membered rings in these glasses in more detail.

Careful inspection of the trigonal unit vibrational band centered at $\sim 800\text{ cm}^{-1}$ in this composition range shows that this band also undergoes some changes. For the glass with $x = 0.35$, this band is a doublet, one mode at 835 cm^{-1} and one mode at 805 cm^{-1} . This doublet likely arises from the A_2'' bending and E' stretching modes of the trigonal units contained in the six-membered ring units. As x approaches 0.5, the mode at 835 cm^{-1} decreases in intensity and is replaced with intensity as a shoulder on the low frequency side of the 805 cm^{-1} mode. This could be assigned to the A_2'' mode of the now forming B3(3) *ortho*-thioborate group. The frequency shift from the high frequency side of the E' mode of the B3(1) group (contained in a *meta*-thioboroxyl ring unit) to the low frequency side of the E' mode of the B3(3) *ortho*-thioborate unit is likely associated with the fact that the bending modes of trigonal units contained in six-membered ring units would be sterically hindered and possibly lie at a higher frequency compared to the being of looses trigonal *ortho*-thioborate groups.

The tetrahedral boron unit band at $\sim 650\text{ cm}^{-1}$ undergoes similar small but significant changes in this high-alkali region. As seen in Fig. 6, the band narrows considerably, FWHM of $\sim 150\text{ cm}^{-1}$ at $x = 0.4$ to FWHM of $\sim 75\text{ cm}^{-1}$ at $x = 0.6$. Such narrowing is generally associated with less disorder in the structural group giving rise to the vibration. In this case, this suggests that the tetrahedral borons are becoming more symmetric and less strained as the glass network around them is being depolymerized through the creation of the trigonal *ortho*-thioborate units. Such behavior has been observed in the other alkali thioborate glass series. Also, the frequency of the tetrahedral boron unit vibration shifts to higher frequencies. This has been observed for the other alkali glasses and likely arises from the narrowing of the peak toward the high frequency side. The intensity of the peak remains significant, even at the end of the glass forming range, and this is seen for the Rb thioborate glasses and suggests that unlike the lighter alkali thioborate glasses, the fraction of tetrahedral borons remains relatively high at the end of the glass forming range. Somewhat surprising is that these higher than expected N_4 values

do not in the case of the Cs thioborate glasses lead to stronger glass formation and hence a wider glass formation region in the high-alkali regions. The Cs glasses stop forming glasses with plate quenching at $\sim 60\text{ mol}\%$ Cs_2S compared to 75 and 80 mol% for the other alkali thioborate glasses.

5.4. Composition dependence of the peak frequencies and areas

Finally, Figs. 8 and 9 show the composition dependence of a few of the more important spectral features described and discussed above. The relative integrated areas for the selected peaks were determined by spectral deconvolution. The deconvolution of spectra were performed using standard commercial software. At this point, the purpose of the deconvolution was to determine the relative area of the absorption bands arising for each of the vibrational modes. The deconvolution was not performed to use it as a technique to provide a more detailed vibrational assignment of the individual modes, this is beyond the scope of the current study, but will be reported on in the

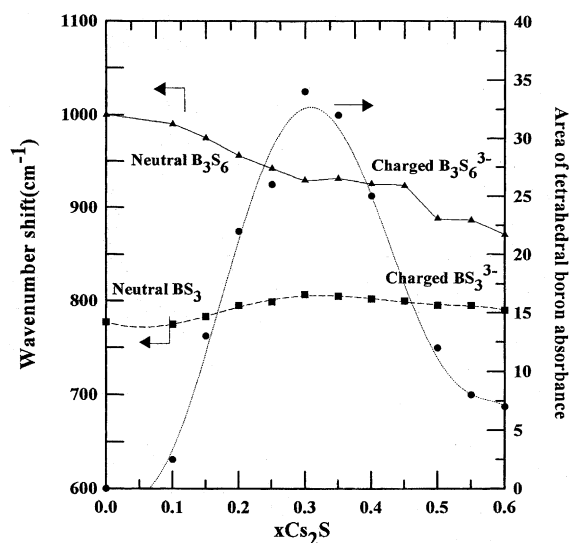


Fig. 9. Composition dependence of the frequencies of the IR absorption bands for trigonal and six-membered ring SRO groups found in $x\text{Cs}_2\text{S} + (1-x)\text{B}_2\text{S}_3$ glasses. For comparison, N_4 determined from ^{11}NMR measurements [34] of the same glasses are also shown.

future. The deconvolution, however, does provide significant quantitative insight into the composition dependence of the various structural groups in the glass and importantly, the range of compositions over which the structural groups persist.

Fig. 8 shows that the relative area of the trigonal mode at $\sim 800\text{ cm}^{-1}$ decreases throughout the compositional range as expected from the model developed here. It also shows that the likely source for the boron to form tetrahedral borons comes from the loose trigonal borons. The relative area for the band from the tetrahedral borons reaches a maximum in the range of $x = 0.30\text{--}0.35$ and decreases thereafter. The relative area for the band of the neutral six-membered ring mode remains relatively constant throughout the low-alkali range where tetrahedral borons are being formed. However, this same area decreases sharply above $x \sim 0.35$ as these neutral thioboroxyl rings are converted to charged six-membered *meta*-thioborate ring groups. Above $x \sim 0.35$, the relative area of the band for the *meta*-thioboroxyl ring units increases strongly as they are formed from neutral rings and from tetrahedral borons that are now decreasing in relative concentration. Finally, the relative area of the band arising from charged *ortho*-thioborate groups increases above $x \sim 0.50$ and is expected to reach 100% of the integrated area as the composition reaches $x \sim 0.75$. As discussed above, though this may not happen due to the propensity of these glasses to maintain higher than expected fractions of tetrahedral borons in the high-alkali region.

In Fig. 9 the frequency shifts of the trigonal units, both neutral (B3(0)) and charged (B3(3)), and the six-membered rings, both neutral ($\text{B}_3\text{S}_3\text{S}_{3/2}$) and charged ($\text{B}_3\text{S}_3\text{S}_3^{3-}$) are plotted along with relative area of the band for the tetrahedral boron units. The frequency of the B6 unit remains relatively constant at $\sim 1000\text{ cm}^{-1}$ out to $x \sim 0.20$, decreases to a plateau value of $\sim 930\text{ cm}^{-1}$ between $x = 0.25$ and 0.4 , and then decreases sharply to $\sim 870\text{ cm}^{-1}$ between $x = 0.5$ and 0.6 . The frequency of the trigonal group on the other hand, increases slightly in frequency, reaches a broad weak maximum and then decreases slightly again to a value just slightly larger than that of the initial value. These three regimes correspond to the three com-

positional regimes described above in the compositional model of the structure of these glasses. In the low-alkali region, the trigonal units are being converted to tetrahedral boron units, so the remaining trigonal and six-membered rings units are largely unaffected by the change. Above $x \sim 0.20$, most of the loose trigonal units are expected to be consumed and alkali now begin attacking the neutral six-membered rings, converting them into both tetrahedral borons and charged *meta*-thioborate rings. The frequency of this mode therefore decreases to a value intermittent between the neutral and fully charged ring values. The frequency of the trigonal group is now affected since these vibrations are now coming from trigonal groups in the six-membered ring units. Finally, in the high-alkali range, the six-membered rings are now fully formed as *meta*-thioborate rings units and exhibit a frequency of $\sim 870\text{ cm}^{-1}$. The trigonal units likewise are becoming fully charged *ortho*-thioborate groups and as such the frequency of this mode reflects the values expected for the *ortho*-thioborate unit, $\sim 800\text{ cm}^{-1}$.

5.5. Refined compositional model of the short range order structures

Having made assignments for all of the SRO structures expected to form in this series, attention is now turned to considering the composition dependence of the fractions of boron atoms contained in these SRO groups. A preliminary model has already been presented and used to model the density of these glasses [31]. This composition plot is shown in Fig. 10. At the time this model was developed, the ^{11}B NMR, neutron diffraction, and Raman spectroscopy experiments had not been performed and as such the trigonal groups in $\nu\text{-B}_2\text{S}_3$ were treated as a single unit independent of whether they were contained in six-membered rings or as isolated trigonal units. It is now known that 75% of the borons are located in six-membered rings and 25% of the borons are located isolated trigonal groups [17]. Hence, Fig. 10 now includes this distinction where for $\nu\text{-B}_2\text{S}_3$ two fractions exist, f_{B3} is the fraction of borons in isolated trigonal groups and f_{B6} is the fraction of borons in six-membered rings (neutral).

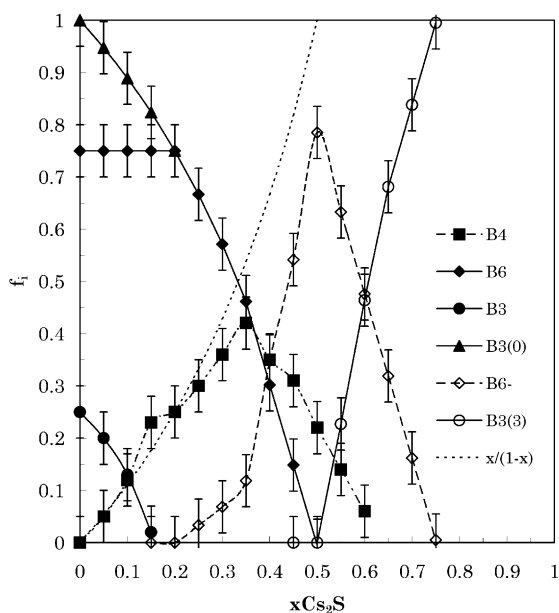


Fig. 10. Refined SRO structural model proposed for the $x\text{Cs}_2\text{S} + (1-x)\text{B}_2\text{S}_3$ glasses as determined from both the IR spectra reported here and the ^{11}B NMR spectra reported previously [34].

The fraction of tetrahedral borons in these glasses has been previously determined and published as discussed above and the f_{B_4} data are plotted in Fig. 10. A dashed line is added to the data to indicate the composition dependence of f_{B_4} expected according to the well-known $x/1-x$ rule where two tetrahedral borons are formed for every added M_2S . The fit to the data is quite good up to $x \sim 0.20$, where after f_{B_4} falls below the $x/1-x$ line and as such suggests that other structural groups are forming in the glass.

As discussed above, the IR spectra suggest that the tetrahedral borons formed in these glasses do so initially at the expense of the isolated trigonal borons in the glass. As a result, the frequency of the six-membered ring mode remains unchanged up to $x \sim 0.20$ and the relative intensity of the isolated trigonal group decreases compared to that of the six-membered ring group. Hence, f_{B_6} is thought to remain constant out to $x \sim 0.20$, with f_{B_3} decreasing in direct proportion to f_{B_4} . Beyond $x \sim 0.20$ all of the isolated trigonal groups will have been converted to tetrahedral borons and the

tetrahedral borons that do form, must do so at the expense of the borons in the six-membered rings.

The fact that f_{B_4} does not quantitatively follow the $x/1-x$ line suggests that a new structural feature must be forming to accommodate for the added Cs_2S . The IR spectra at this compositional point as seen in Fig. 5 and discussed above, show a distinct frequency shift to lower frequencies towards that of the *meta*-thioborate six-membered ring. This suggests that the added Cs_2S beyond $x \sim 0.20$ not only creates more tetrahedral borons since f_{B_4} continues to increase out to $x \sim 0.35$, but that it also creates *meta*-thioborate groups with the fraction of Cs_2S that is not used to create tetrahedral borons. Hence, $f_{\text{B}_6}^-$, the fraction of charged six-membered *meta*-thioborate rings, begins to increase at $x \sim 0.20$ but only a relatively small rate.

Between $x \sim 0.20$ and 0.30 , the mode arising from *meta*-thioborate group broadens as its structure is being converted from neutral thioboroxyl rings to charged *meta*-thioborate groups. Beyond $x \sim 0.30$, this mode narrows again as a result of the *meta*-thioborate structural group developing more fully in the glass structure. The intensity of the trigonal group does not decay to zero as might be expected in the compositional range because the six-membered rings possesses trigonal groups and might be expected to give intensity for this band at this frequency. It is significant to note that beyond $x \sim 0.20$, the frequency of the trigonal group increases slightly, perhaps as a result of the tighter bonding constraints of the trigonal groups located in six-membered rings.

Fig. 10 shows that $f_{\text{B}_6}^-$ increases more rapidly beyond $x \sim 0.35$ and reaches a maximum as suggested by the IR spectra at $x = 0.5$. As also shown from the IR and ^{11}B NMR spectra, f_{B_4} reaches a maximum at 0.35 and decreases to zero in the vicinity of $x = 0.65$. This behavior of f_{B_4} is quite different from that of all the other alkali thioborate glasses. f_{B_4} does not reach zero in all the other alkali thioborate glasses until $x \sim 0.75$, the *ortho*-thioborate composition. The result that f_{B_4} reaches zero earlier in composition than $x = 0.75$, implies that either $f_{\text{B}_6}^-$ can remain higher at higher x or that the fraction of borons contained in the *ortho*-thioborate groups, $f_{\text{B}_3(3)}$, can begin to increase at a lower composition. It is not entirely clear which of

these two hypotheses is the correct one, but some evidence for the latter can be obtained from the IR spectra of the Rb thioborate glasses.

The Rb thioborate glasses can be prepared out to $x = 0.75$ and their IR spectra show that the *meta*-thioborate group persists in high fraction even out to $x = 0.75$ (see Fig. 5 of Ref. [2]). Additionally, on close inspection of the IR spectra of the high-alkali Cs_2S glasses, it is seen that it is not until $x = 0.6$ that there is any change in the frequency and band shape for the trigonal mode located at $\sim 800\text{ cm}^{-1}$. This suggests that the *ortho*-thioborate group does not form at lower composition, but rather forms beyond $x = 0.5$ as expected from stoichiometry.

From this discussion then, the proposed composition dependence of the fraction of borons contained in the five SRO groups observed in these glasses is shown in Fig. 10. Of significant note is the lack of the formation of either neutral four-membered rings in $\nu\text{-B}_2\text{S}_3$ or charged four-membered *meta*-thioborate rings in the compositional vicinity of $x = 0.5$ as might be expected since the Cs *meta*-thioborate crystal possesses this structure. It is not clear at this point why these four-membered rings fail to form in these glasses. One possibility is that these rings are expected to be highly strained and perhaps in the crystal structure such strained units can exist, but in the looser, more open, and relaxed structure of the liquid and glass, these units open to less strained structures, namely the isolated trigonal unit for the former and the six-membered *meta*-thioboroxyl ring units for the latter. This might also explain the higher than stoichiometric amount of the B6^- group.

Additional unanswered questions that remain at this point are what is the exact crystal structure of the Cs dithioborate phase and why does the pyro-thioborate group, B3(2), fail to form in all of the alkali thioborate glasses? For the former question, detailed XRD studies are in progress to explore the nature and structure of this phase and will be reported on in the future. For the latter question, careful studies have been made of the composition at which this phase would be expected to form, $x = 0.66$, and as yet no congruent phase has been observed. The IR spectra of polycrystals at this composition yield a composite IR

spectra of the B6^- group and the B3(3) group. It appears that this structure does not form in these series. Other studies of other metal thioborate phases, $\text{Ag}_2\text{S} + \text{B}_2\text{S}_3$ in particular, are in progress to see how general this behavior and also will be reported on in the future.

6. Conclusions

$x\text{Cs}_2\text{S} + (1-x)\text{B}_2\text{S}_3$ glasses and polycrystals, $0 < x < 0.6$ have been prepared and their IR spectra have been investigated for the first time. In the low-alkali glasses, $x < 0.35$, the IR spectra of the cesium thioborate glasses are analogous to those of the sodium, potassium, and rubidium thioborate glasses where the monotonic increasing fraction of tetrahedral borons is observed. Like the other alkali thioborate glasses, the tetrahedral borons appear to form from the trigonal boron units rather than the thioboroxyl ring units. In the high-alkali region, $x > 0.50$, the IR spectra indicate the decreasing fraction of the *meta*-thioborate and tetrahedral boron groups and the simultaneously increasing fraction of the *ortho*-thioborate groups. Quite surprising is finding that while the Cs *meta*-thioborate crystal structure has been shown to consist of unique four-membered rings, similar to those found in crystalline B_2S_3 , no evidence can be found of the four-membered *meta*-thioborate ring unit in the Cs doped glasses, even near $x \sim 0.50$, where this phase would be expected to most prominent. Rather, the IR spectra of these glasses strongly suggest that these glasses form the six-membered *meta*-thioboroxyl ring unit in similarity to the other alkali thioborate glasses. A plausible reason to understand this behavior is provided.

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