VIBRATIONNAL SPECTRUM OF TRISODIUM CALCIUM PENTABORATE Na$_3$Ca(B$_5$O$_{10}$) AND PROBABLE OCCURRENCE OF THE DISCRETE PENTABORATE ION (B$_5$O$_{10}$)$^{5-}$ IN SOME GLASSY METABORATES

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Résumé : Les spectres IR et Raman de l'ion pentaborate (B$_5$O$_{10}$)$^{5-}$ «isolé» (présent dans le composé Na$_3$Ca B$_5$O$_{10}$) sont présentés et discutés en relation avec la présence éventuelle de cet ion dans certains verres de composition métaborate (ou proche).

La présence de l'ion pentaborate «isolé» dans les verres est étayée par la forte analogie qui existe entre les spectres IR de Na$_3$Ca B$_5$O$_{10}$ cristallisé et vitreux. De même, le spectre Raman de Na$_3$Ca B$_5$O$_{10}$ cristallisé montre à 576 cm-1, un intense pic caractéristique que l'on retrouve aussi dans les spectres Raman des métaborates M$^+$BO$_2$ (M$^+$ = Na...Cs) vitreux publiés dans la littérature On en déduit que l'ion pentaborate (B$_5$O$_{10}$)$^{5-}$ «isolé» peut être une des unités structurales présentes dans ces types de verres. Cet ion disparaît rapidement et est remplacé par d'autres unités structurales :

1. Lorsque le rapport cation/anion est très différent de celui de la composition métaborate.

2. Lorsque pour une composition métaborate la nature chimique des cations est telle que les liaisons cation – oxygène ne sont pas fortement ioniques.

Mots-clés : ion pentaborate, composition, métaborate, unité structurale, spectres IR, Raman

I - INTRODUCTION

Since the initial work by Krogh-Moe on the IR spectrum of borates, numerous papers have been devoted to the study of the vibrational spectrum (IR and Raman) of crystalline and glassy borates, one of the main goals of such studies being the identification of the structural

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units existing in the glasses (see e.g.[1-3]). Recent work in this field has evidenced an unexpected diversity of structural units, even in glasses with a simple metaborate composition M^+BO_2 (M+ = Li, Na...Cs) : the Raman spectra are interpreted by the coexistence of a number of structural units going from complex associations of BO_3 and BO_4 groups to isolated pyroborate $(B_2O_5)^{4-}$ ions [3]. We show here that the discrete pentaborate ion $(B_5O_{10})^{5-}$ (existing in the structure of $Na_3Ca\ B_5O_{10}$ [4], but never considered in previous work on glassy borates) is a probable structural unit of such glasses.

II - EXPERIMENTAL

Synthesis of both the compounds and glasses

The compounds $Na_3CaB_5O_{10}$ and $Na_3SrB_5O_{10}$, together with inter-mediate compositions Na_3 (Ca1-x Srx) B_5O_{10} were synthesized by convèntionnal solid state reaction techniques.

The stoichiometric quantities of the reagents ($NaHCO_3$, $CaCO_3$, $SrCO_3$, H_3BO_3, all of analytical purity) are well ground and mixed, and very progressively heated in covered platinum crucibles, first to 200°C, and then slowly up to 800°C with intervening mixing and grinding. This final temperature is maintained for 2 or 3 days, until no modification is observed in the x-ray diffraction pattern.

The formation of glasses was attempted by melting a small quantity of prereacted powder on a platinum sheet at about 1100°C, and air – or oil-quenching. Only thin flakes were obtained : we were unable to prepare bulk quantities of these glasses. The lack of crystalline phases in the resulting glass was checked by x-ray diffraction.

III - RESULTS AND INTERPRETATIONS

Differential thermal analysis of vitreous $Na_3Ca\ B_5O_{10}$

The DTA curve exhibits nearly at 490°C an exothermic peak corres-

ponding to the crystallisation of the glass (leading to crystalline Na_3Ca B_5O_{10}), and a broad endothermic event nearly at 850°C due to the incongruent melting of the compound.

X-ray diffraction

So far, the discrete pentaborate ion $(B_5O_{10})^{5-}$ has been evidenced only in the structure of $Na_3CaB_5O_{10}$ [4]. We have accordingly investigated the possibility to replace the Ca_2+ cation by either Sr^{2+} or Cd^{2+}. X-ray powder diffraction shows that the Ca^{2+} and Sr^{2+} compounds are isomorphous, with a continuous series of solid solutions $Na_3(Ca_{1-x}$ $Srx)B_5O_{10}$. Solid solutions $Na_3 (Ca1-x\ Cdx)B_5O_{10}$ can also be prepared, but only in a limited range ($0 < x < 0.75$). The existing results do not allow to decide whether the composition $Na_3CdB_5O_{10}$ corresponds to a definite compound or to a mixture. Additional work on these cationic replacements is presently going on and the results will be published later on.

Infrared spectrum of crystalline $Na_3CaB_5O_{10}$

The strongest bands appearing in the 1500-700 cm^{-1} range (Fig. 1) can be more or less arbitrarily distributed over four spectral regions, namely 1500-1350, 1250-1200, 1100-900 and 800-700 cm^{-1}. All these bands exhibit a significant ^nB-^{10}B isotopic shift (Table 1 ; ^nB stands for boron with natural isotopic composition, namely 81.17 mol% of ^{11}B ; ^{10}B stands for boron containing 94 mol% ^{10}B). In view of both the complexity and low symmetry of the structure, it is not possible to propose detailed assignments for the individual bands. But consideration of the B-O distances, and comparison with the spectra of other appropriate borates lead to a reasonable interpretation of the different absorption regions.

Raman ^nB Na$_3$Ca(B$_5$O10)	^{10}B	Infrared ^nB Na$_3$Ca(B$_5$O10)	^{10}B	Na$_3$Sr(B$_5$O10) ^nB
1535 vw		1475 s	1525	1455
1495 s	1543			
1430 vw				
1397 w	1440	1395 s	1448	1395
1294 w	1333	1336 vw	1353	1318
1232 vw	1263	1212 s	1248	1235
		1185 s	1217	1200
		1080 vw		1082
		1053 s	1080	1057
		1016 s	1026	1030+ 1017
950 vw,sh	966	948 s	955	936
	948			
938 s	937			
922 w		920 s	935	920
785 w	795	784 s	794	776
762 m	778	754 w	760	753
	757			
753 vw	750	717 s	734	723
695 m	720	708+701 w	703	708 + 698
629 mw	633	627 w	635	628
617 w				
576 vs	583	580 vw	585	
519 m	522	513 vw	516	508
484 m	486	480 vw	483	
374 vw	372	390 m	390	415+ 385
316 vw	317	320 m	320	
290 vw	291			
279 vw	278	not investigated		
226 w	224			

The frames indicate the strong Raman bands which are also observed in the Raman spectra of glasses with or near a metaborate composition.

TABLE 1 : *Vibrational spectrum of the pentaborate ion* $(B_5O_{10})^{5-}$

Figure 1 : *Infrared spectrum of crystalline (full line) and glassy (dashed line) Na_3Ca (B_5O_{10}).*
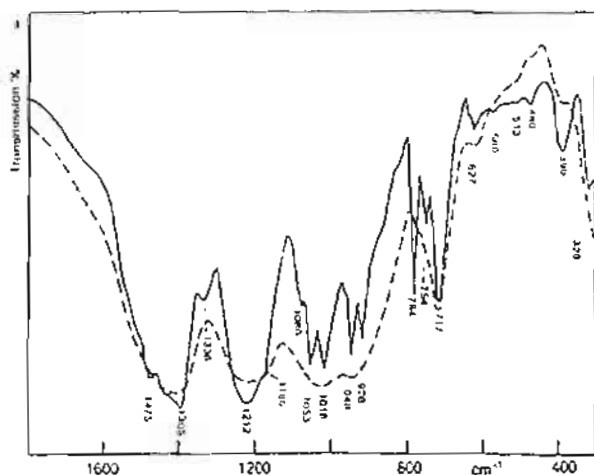
The frames indicate the strong Raman bands which are also observed in the Raman spectra of glasses with or near a metaborate composition.

Some relevant data are collected in table 2. They show that the condensation of BO_3 triangles, into either chains or rings, leads to two types of B-O bonds and of B-O distances, namely short B-O– bonds (oxygen bonded to a single B atom, or non-bridging oxygen, the negative charge being compensated by the neighbouring cations), and longer B-O-B bonds (labeled B-O bridging). The corresponding B-O stretching frequencies are accordingly split into two bands or groups of bands, centred near 1400 and 1200-1100 cm^{-1}. Still longer bonds and lower frequencies are found for the BO_4 tetrahedra (as examplified in Table 2 by Fe_3BO_6). These three regions appear clearly in the IR spectrum of crystalline $Na_3CaB_5O_{10}$ (Fig. 1 and table 1) and of isomorphous $Na_3SrB_5O_{10}$.

These three possibilities are also represented in the pentaborate-hydrate anion $[B_5O_6 (OH)_4]^-$ existing, e.g. in K $[B_5O_6(OH)_4]$. $2H_2O$[8]. However, the vibrational behaviour of this hydrated anion[9] is somewhat different from that of the corresponding anhydrous anion $(B_5O_{10})^{5-}$ considered in this paper for at least two reasons :

- The external B-O- groups of the anhydrous anion are replaced, in the hydrated anion, by B-OH groups in which the B-O distances are slightly, but significantly longer (probably in relation with the partial covalent character of the O-H bond).

- The vibrational frequencies of the B-O stretching and of the B-OH bending motions are of the same order of magnitude and can be more or less strongly coupled, as demonstrated by the study of the deuterated anion [9].

TABLE 2 : *Correlations between the types of B-O bonds, B-O distances and B-O IR stretching frequencies*

Compound	Types of B-O bonds	B-O distances ()	$V (cm^{-1})$	Réf.
LiBO₂ Chain of BO3triangles	B-O – B-Obridge	1.33 1.38-1.40	1400 1150-1100	[5]
- Ba₃ (B₃O6)₂ B₃O₆ rings of BO₃ triangles	B-O – B-Obridge	1.32 1.40-1.41	1400 1250	[6]
Fe₃BO₆ discrete BO₄ tetrahedra	B-O –	1 50 (x3) and 1.44	860+826 1025	[7]
Na₃CaB₅O10 discrete (B₅O10)⁵⁻ pentaborate ions	B-O – in BO₃ B-Obridge in BO₃ B-Obridge in BO4	1.31 1.395 1.47	1400 1200 1000	[4]
K [B₅O₆ (OH)₄]. 2H₂O Hydrated pentaborate ions [B₅O₆(OH)₄]⁻	B-OH B-Obridge in BO₃ B-Obridge in BO₄	1.35-1.36 1.35-1.38 1.47-1.48	1360 1250 1000	[8]

The bands of the 800-700 cm^{-1} region are due, at least in part, to bending motions (in plane and out of plane) of the B_3O_6 rings [9], but the complexity of the pattern is much greater than that observed in the spectrum of $Ba_3 (BO_2)_6$ (whose structure also contains (B_3O_6) rings, but not BO_4 tetrahedra).

The lower-frequency bands are weak and even very weak. The band at 320 cm^{-1} in the spectrum of the Ca compound is missing in the spectrum of the Sr compound ; this suggests its assignment to a Ca^{2+} translation, in agreement with previous results on CaB_2O_4[5] and $Ba_2Ca(B_3O_6)_2$[6].

Raman spectrum

As far as the relative intensities are concerned, the general presentation of the Raman spectrum is rather different from that of the IR spectrum, with only three strong bands (plus a number of bands of weak to medium intensity) at 1495, 938 and 576 cm^{-1} (Fig. 2). The first one, with a large 10B-nB isotopic shift (1543-1495 cm^{-1}) is clearly due to a B-O- stretching vibration. The 938 cm^{-1} band exhibits no significant 10B-nB frequency shift (Table 1) : it has been tentatively assigned to a motion more or less similar to the totally symmetric mode V1 of the free $(BO_3)^{3-}$ anion : a similar, very strong band is observed at 919 cm^{-1} in the Raman spectrum of the hydrated pentaborate ion $[B_5O_6(OH)_4]^-$ [10]. This assignment is however an approximation, since no strong band is observed in the Raman spectra of the metaborates BaB_2O_4 and $Ba_2M_2+ (B_3O_6)_2$ (M^{2+} = Mg, Ca, Cd), whose structure contains also (BO_3) groups forming $(B_3O_6)^{3-}$ ring anions : these compounds exhibit only weak to very weak bands in the same spectral region [6]. Thus, the existing results suggest that the large intensity of this band is correlated with the occurrence of BO_3 groups in some specific ring structures, probably containing also BO_4 groups.

The 576 cm^{-1} band (583 cm^{-1} in the 10B borate ; 567 cm^{-1} in the Sr compound) is the strongest of the spectrum. A similar, very strong Raman band is observed in the 560-550 cm^{-1} region for different compounds containing the hydrated pentaborate ion $[B_5O_6(OH)_4]^-$ [10, 11]

A definite assignment of this band has been considered difficult (as it is generally the case for fairly low frequencies exhibited by complex anions) in some previous papers.

It has been first assigned to some vibration of isolated diborate groups containing non-bridging oxygen [11], or to some bending (out of plane) vibration of the BO_3 group in the ring [10]. Kamitsos et al. [12] have pointed out the considerable interest of the 600-450 cm^{-1} region for the structural study of borate glasses, and the complex origin (diborate, triborate, pentaborate groups) of the bands observed in this frequency range. For alkali glasses with (or near) the metaborate composition, a strong Raman band is observed near 550 cm^{-1} ; it is tentatively assigned to the symmetric stretching vibration of « loose » BO_4 tetrahedra [13], i.e. «Tetrahedra connecting various segments without participating in specific borate arrangements»[14].

FIGURE 2 : *Raman spectrum of crystalline Na$_3$Ca (B$_5$O$_{10}$)*
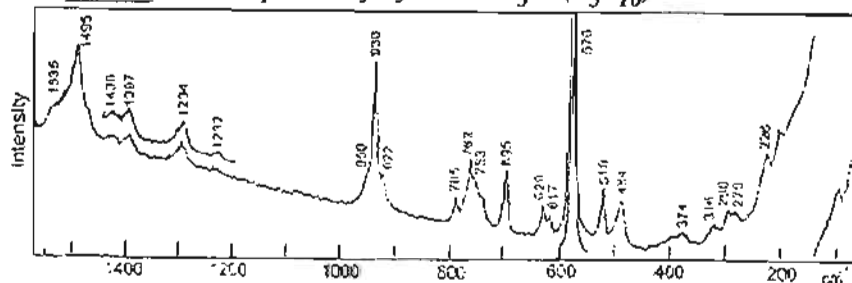
Finally, a precise, very interesting assignment has been proposed by Janda and Heller [11] on the basis of the great intensity, of the small 10B- 11B isotopic shift, and of the zero value of the depolarization ratio

of this band : this frequency could be assigned to the breathing vibration («Pulsationsschiwingung» in the german paper) of the whole ion.

This assignment is also in agreement with other experimental results :

1) A similar band is observed at a somewhat higher frequency (about 576 cm $^{-1}$) in the Raman spectrum of borax $Na_2B_4O_7.10\ H_2O$, whose structure contains discrete hydroxyl tetraborate ions $[B_4O_5\ (OH)_4]^{2-}$ [12]. Here again, this band is, by far, the strongest of the spectrum [1]. The slightly higher frequency is possibly related to the smaller size of the ion. On the contrary, this band disappears completely in the spectrum of $Li_2B_4O_7$, whose structure contains also (B_4O_9) groups, but where these groups are interconnected to form a highly polymerized structure [1].

2) Likewise, the Raman spectrum of other compounds whose structure contains interconnected pentaborate groups (e.g. $K_2O.5B_2O_3$) do not exhibit a strong band in the 550 cm^{-1} region (a series of relatively weak bands is observed in the 550-450 cm^{-1} region) [1].

A series of more complex examples will be found in [1] : they are in agreement with the above-mentioned results : polyborates whose structure contains highly interconnected groups never give a characteristic, very strong Raman band in the vicinity of 550 cm^{-1}. This is consistent with the assignment of this band to a breathing vibration : such a characteristic motion is conceivable in the case of a discrete ion of moderate size, but is probably impossible in a highly polymerized, geometrically complex lattice.

Spectra of the glasses

IR spectra : The IR spectra of crystalline and viterous $Na_3CaB_5O_{10}$ are represented in figure 1. The spectrum of the glass appears as the envelope of the spectrum of the crystal and, from this analogy, we can assume that a significant amount of discrete pentaborate ions has been preserved in the vitreous structure.

Raman spectra : Despite several attempts with different laser wave-lenghts (488.0 and 514.5 nm lines of an Ar^+ laser ; 632.8 nm line of a He-Ne laser), we were unable to obtain a satisfactory Raman spectrum because of a very strong background which persisted after very long laser irradiation.

We can, however, gain some information from the Raman spectra published in the literature and, more precisely, from the presence or the absence, in the spectra, of a strong band in the vicinity of 550 cm^{-1}.

A first example is given by a series of glasses of general composition $x\,M^+_2O.(1-x)B_2O_3$ ($M^+ = Li + Na + K + Cs$; x = 0.40, 0.45, 0.48 and 0.52 ; x = 0.50 (not investigated) would correspond to an ideal meta-borate composition) [1]. For x = 0.40, the Raman spectrum exhibits a band of medium intensity at 525 cm^{-1}. But for increasing values of x (0.45 and 0.48), the intensity and the sharpness of this band increase strongly, whereas its frequency is shifted near 560 cm^{-1}. For the x = 0.48 composition, this band is by far the strongest of the spectrum ; moreover, measurements in polarized light show it is strongly polarized. Its relative intensity is still very strong (but begins to decrease) for x = 0.52. Thus, this band presents its maximum intensity near the metabo-rate composition, and its properties (frequency, intensity and polariza-tion) are very similar to those already observed for the pentaborate ion, either hydrated [10] or anhydrous (this paper).

A similar behaviour is observed in the Raman spectra of glasses x $Na_2O. (1-x)B_2O_3$ (0.35 < x < 0.75) [12]. Starting from x = 0.35, there is first an increase in frequency and intensity of the band (s) observed in the 600-500 cm^{-1} region, with a maximum of intensity correspon-ding to x = 0.50 (metaborate composition). For x > 0.50, this intensity decreases and the bands disappear completely for x = 0.67.

Another example is given by the spectra of the vitreous alkali meta-borates $M^+ BO_2$ ($M^+ = Li, Na...Cs$) [15]. Apart from $LiBO_2$, whose vibrationnal behaviour is peculiar, the Raman spectra of all alkali

metaborates exhibit their strongest low-frequency peak in the 570 - 550 cm⁻¹ region.

Thus, both infrared and Raman data suggest the presence of discrete pentaborate ions in alkali glasses with (or near) a metaborate composition.

IV - DISCUSSION

The occurrence of discrete pentaborate ions in the structure of vitreous metaborates had never been considered before, and it is worth while to compare this assignment with those proposed previously for vitreous alkali metaborates, and more precisely for Na and Cs metaborates, which have been discussed in specific papers [12,13]. These assignments are collected in Table 3.

TABLE 3 : *Previous and proposed assignments for Raman frequencies of vitreous NaBO₂ and CsBO₂*

NaBO₂ [12]		CsBO₂ [13]	Proposed
545	isolated diborate	545 vs loose BO_4	Pentaborate ion
570	s «loose» BO_4		$(B_5 O_{10})^{5-}$
630 m	metaborate ring	606 m metaborate ring	Pentaborate (in part)
690 vw	metaborate ring		Pentaborate (in part)
757 ms	rings containing BO_4 unit(s)	755 m	Pentaborate (in part)
820 vw	pyroborate ion	795 vvw pyroborate ion	Not Pentaborate
940 ms	loose diborate	900 m loose BO_4	Pentaborate (in part)
		1240 w pyroborate ion	Not Pentaborate
1490 s groups	B-O- in several borate	1490 m B – O- in metaborate rings	Pentaborate (in part)

The two regions 570 - 545 and 940 - 900 cm^{-1} have been assigned to either «loose» BO_4 tetrahedra or «loose» diborate groups. The first assignment is fairly vague since, according to Konijnendijk, «loose» BO_4 groups are tetrahedra which possess all bridging oxygens, and connect different borate segments (Note that, according to this definition, the discrete pentaborate ion of our assignment is in fact a peculiar case of loose BO_4 tetrahedra).

The second assignment is based on the fact that the Raman spectrum of the hydrated diborate ion $[B_4O_5 (OH)_4]^{2-}$ (existing in borax $Na_2B_4O_7.10H_2O$) exhibits strong bands at 947 and 576 cm^{-1} [11, 12]. Nevertheless, we must notice that these results have been obtained with the hydrated ion, and that reference data on the corresponding anhydrous ion are missing (in fact, the anhydrous ion with an equivalent structure would be $(B_4O_9)^{6-}$, and the corresponding sodium salt $Na_6B_4O_9$, far from a mataborate composition. Another point to be emphasized is the great sharpness of the 545 cm^{-1} band of the Cs glass : this suggests its assignment to a well-defined structural group, which could be the pentaborate ion.

On the contrary, the 950-900 cm^{-1} band is not so sharp and could result from the superposition of the band(s) of several structural groups (including the pentaborate ion).

The remaining bands are less characteristic. By its intensity, the strong 1495 cm^{-1} band indicates significant amounts of B-O- (non-bridging) bonds in ring structures, but does not give precise information about the nature of the structural units containing these B-O- bonds.

The pentaborate ion may also contribute to the bands near 760-750 and 630-600 cm^{-1}, but the intensity of these bands is too high to be interpreted by the pentaborate ion alone : a contribution from other structural units (e.g. metaborate or more complex ring structures containing one or two BO_4 tetrahedra) must also be considered [12, 13].

These interpretations can be extended to vitreous K and Rb metaborates [15], but not to vitreous Li metaborate [16], since its Raman spectrum is essentially characterized by important changes in the broadness and in the relative intensities of the bands. These results (which do not exclude the presence of pentaborate ions) can be interpreted by an increase of the number of ring configurations containing one or two BO_4 tetrahedra.[17]. This is in agreement with the conclusions of Zhong and Bray [18] deduced from the 11B NMR study of $xM^{2+}O. (1-x)B_2O_3$ glasses (M^+ = Li, Na...) : for a given value of x and particularly in the compositional range $0.3 < x < 0.5$, the fraction of boron atoms in fourfold coordination is the highest for the Li glass, and decreases in the sequence Li-Na-K-Rb-Cs.

Glass-forming properties of metaborates

The glass-forming region of the $x Na_2O. (1-x)B_2O_3$ system exhibits a gap for $0.40 < x < 0.66$.[19] and, near the metaborate composition (x = 0.50), no glass could be prepared even at the very high cooling rates obtained by the roller quenching technique [20, 21]. This gap can be removed by the addition of a relatively small quantity of Al_2O_3 [12,22,23]. Likewise, the addtion of non-negligible quantities (10 mol%) of Al_2O_3 is required to prepare vitreous KBO_2 and $RbBO_2$[15]. This gap does not exist in the system $Li_2O.B_2O_3$ [24], but in that case, the infrared spectrum suggests the existence, in the glass, of LiO_4 tetrahedra [25] which should stabilize the glassy structure, whereas the Raman data show important structural changes with respect to the other alkali metaborate glasses [16, 17].

More or less similar trends are observed in the case of $M^{2+}O.B_2O_3$ metaborates : no glass could be obtained for M^{2+} = Ba, and rapid quenching was necessary to obtain vitreous SrB_2O_4 and CaB_2O_4 [26] ; but the formation of a glass was easier for MgB_2O_4, and much for PbB_2O_4. This should be related to the less ionic character of the Mg-O

and Pb-O bonds. In the case of PbO-B_2O_3 glasses, the far IR spectrum shows the existence of pyramidal, covalent Pb-O bonds (the 6s2 electronic pair of the Pb^{2+} ion is stereochemically active) [27]. On the other hand, results of 11B NMR studies of glasses in the system $MgO-Na_2O-B_2O_3$ have been interpreted by the formation of MgO_4 tetrahedra when the molar fraction of MgO is greater than 0.15[28]. Likewise, far IR spectra of metaborate glasses Ba_2M^{2+} $(B_3O_6)_2$ show the existence, for $M^{2+} =$ Ni, Co or Zn, of a significant amount of $M^{2+}O_4$ tetrahedra [29]. These tetrahedral groups should participate in the stabilization of the vitreous phase.

Now, it is interesting to compare these results with the Raman spectra exhibited by glassy metaborates x $MgO.y$ $Na_2O.B_2O_3$ $(x + y = 1)$ [30]. For $x = 0.47$, the Raman spectrum exhibits at 570 and 940 cm^{-1} broad bands which could contain a contribution from the pentaborate ion; but for $x = 1$ (Mg metaborate), the 570 cm^{-1} band has completely disappeared, and the 940 cm^{-1} band is replaced by a broad, very weak shoulder. This illustrates clearly, for an overall metaborate composition, the structural influence of the replacement of a monovalent alkali cation by a smaller, divalent cation[30].

We can now bring together the following features, applicable to glasses with a metaborate composition.

1) The ease with which (a) glass is formed depends largely on the chemical nature of the cation(s). The formation of a glass is difficult, say even impossible, with cations giving essentially ionic bonds with oxygen, namely alkali and alkaline-earth cations with a relatively large ionic radius (Na – Cs ; Ca -- Ba).

2) The results presented and discussed in this paper suggest that discrete pentaborate ions could be an essential structural unit for these glasses. Thus, despite its size, the pentaborate ion appears as a very structural unit bad for glass forming. This can be understood as follows : owing to its structure (two nearly planar six-membered rings connec-

ted by a common BO_4 tetrahedron [4]), the pentaborate ion is probably characterized by a fairly rigid configuration, and this lack of flexibility is certainly unfavourable to the formation of a glass.

3) On the contrary, the formation of a glass is easier with cations characterized by a smaller size and / or a higher charge, thus giving less ionic bonds with oxygen. In such cases, the formation of a glass is enhanced by the simultaneous influence of two factors :

i. For the published Raman spectra exhibit, either an important broadening of the 550 cm^{-1} band (e.g. $LiBO_2$ [16]), or the complete disappearance of this band (e.g. MgB_2O_4 [30]. It may be inferred that the discrete pentaborate ions are partially or totally destroyed, most probably through the transformation of some (BO_3) into (BO_4) groups and the formation of larger structural units ;

ii. And some cations at least, a non-negligible fraction of them can act as glass formers by taking a tetrahedral coordination.

Finally, it is also interesting to note that, in a system such as $xNa_2O.(1-x)B_2O_3$, the difficulty to obtain a glass is the greatest with the metaborate composition ($x = 0.50$) : the formation of a glass is easier with small x values (as expected), but also higher x values, leading, e.g. to a pyroborate composition [12]. This last trend is somehow unexpected, since greater x values lead to smaller ionic fragments and a supposed decreasing ability to form a glass. However, this is understandable if we assume that the pentaborate ion is a bad glass former because of its relative rigidity. For x 0.50, this anion disappears fairly rapidly (as shown by the decrease of its characteristic Raman band near 570-550 cm^{-1} and is replaced by smaller ions, mainly the pyroborate ion $(B_2O_5)^{4-}$ for $x = 0.65-0.67$ [12].

Despite its smaller size, this anion is able to take various configurations (see, e.g. [31]), and this should have a favourable influence on the formation of glasses.

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