Nouveaux verres borophosphates de sodium et de calcium. Corrélation structure-propriétés physico-chimiques. Application dans le domaine biomédical

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PRESENTEE A

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DOCTEUR

SPECIALITE : SCIENCES DES MATERIAUX

PAR

Jean - François DUCEL

Nouveaux verres borophosphatés de sodium et de calcium. Corrélation structure - propriétés physico - chimiques. Application dans le domaine biomédical.

Soutenue le 23 Juin 1993

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- 1993 -

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CONCLUSIONS GENERALES *131*

Ce travail a été effectué au sein du Laboratoire de Chimie du Solide du C.N.R.S. de l'Université de BORDEAUX I.

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INTRODUCTION GENERALE

La mise au point et l'étude de nouveaux matériaux utilisables dans le domaine médical fait, de nos jours, l'objet de recherches nombreuses et variées. Couramment désignés par le terme de *biomatériaux*, ils peuvent être définis comme l'ensemble des matériaux soumis à des contraintes biologiques. En conséquence, ils ne doivent pas être toxiques, ni cancérigènes ou induire des réactions de rejet. L'ensemble de ces propriétés peut être défini sous le terme de *biocompatibilité*.

Les prothèses utilisées actuellement en restauration osseuse et dentaire sont réalisées à l'aide de matériaux existant sur le marché. Il s'agit de *métaux et d' alliages métalliques*, de *matériaux organiques* (polymères), *inorganiques* (céramiques, verres et vitrocéramiques) ou bien de *matériaux mixtes* (composites). Ils sont, *en principe*, biocompatibles, mais *dans la pratique*, ces biomatériaux sont imparfaits [1].

A partir des expérimentations cliniques développées ces dernières années, les matériaux inorganiques contenant des phosphates semblent très prometteurs. En effet, de part leur composition chimique proche de celle des tissus osseux, les prothèses phosphatées implantées, sont rapidement colonisées par les cellules osseuses, entrainant la reconstitution d'un ensemble mixte biomatériau-os dont les propriétés seront voisines de celles de l'os original. Ces biomatériaux peuvent être regroupés en deux familles: *les céramiques et les verres et vitrocéramiques.*

La nature vitreuse de ces derniers présentent beaucoup d'avantages liés à la facilité d'élaboration et de mise en forme et à la grande diversité de compositions chimiques permettant d'obtenir, pour chaque type d'application, les propriétés recherchées (dureté, insolubilité, résistance à la compression ou au cisaillement, adéquation avec le milieu environnant ...). Malgré ces multiples attraits, seuls quelques verres multicomposants silicophosphatés et phosphatés de calcium ont été étudiés [2] . Les premiers, de composition assez proche des silicates (très faible proportion en phosphate), possèdent des températures de transition vitreuse (Tg) relativement élevées

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[1] J. Jozefonvicz et M. Jozefonvicz, "Les Biomatériaux" dans *La Recherche*, n°134, (13), 708-718, (1982).

[2] J. J. Videau et V. Dupuis, "Phosphates and Biomaterials" *Eur. J.Solid State Inorg. Chem.*, 28, 303-343, (1991)

(Tg>600°C). Les seconds ont le double avantage d'avoir une composition chimique proche de celle de la partie minérale osseuse et un Tg modéré. En contrepartie, leur structure de type métaphosphate les rend chimiquement moins stables (solubilité) que les verres silicatés.

En vue d'une application biomédicale particulière, les matériaux recherchés devaient répondre aux critères suivants:

- vitrification aisée
- températures de fusion et de transition vitreuse modérées,
- propriétés chimiques et mécaniques convenables (solubilité faible en milieu aqueux),
- compatibilité optimale avec le milieu vivant.

Parmi les composés à fort pouvoir vitrifiant: silicate, métaphosphate ou borate, aucun ne satisfait pleinement à ces quatre critères. Un compromis pouvait être trouvé en associant deux ou plusieurs composants.

L'association de $Na_2B_4O_7$ à $NaPO_3$ nous a semblé une voie d'investigation prometteuse. Les verres formés pouvaient, à priori, présenter les propriétés requises. Néanmoins, dans le but d'optimiser ces matériaux, tant d'un point de vue physico-chimique que de la biocompatibilité, un troisième composé a été ajouté: l'hydroxyapatite de calcium ($Ca_5(PO_4)_3OH$) connu pour être le constituant minéral principal des tissus osseux.

L'étude de ces matériaux, présentée sous la forme de sept publications, s'est déroulée de la façon suivante:

La première partie, qui constitue le Chapitre I, est consacrée aux caractérisations physico-chimiques et structurales des verres issus du pseudo-binaire $NaPO_3$ - $Na_2B_4O_7$. Afin d'expliquer l'évolution inattendue de certaines propriétés, telles que, les températures de transition vitreuse (Tg) et de cristallisation (Tc), la masse volumique (ρ), le volume molaire (V), la microdureté (H_V), la solubilité (S) et la longueur d'onde de coupure dans l'UV (λ_c), des caractérisations structurales par RMN (^{31}P MAS et ^{11}B), absorption IR et diffusion Raman ont été entreprises.

La RMN (^{31}P MAS et ^{11}B) nous a permis d'identifier les différents types d'environnement des atomes de bore et de phosphore présents dans ces verres.

Par ailleurs, les spectroscopies Raman et IR nous ont aidé à connaître l'arrangement des différentes unités phosphatées et boratées, permettant ainsi de mettre en évidence l'existence de groupements borophosphatés inusuels participant à l'édifice vitreux. Des modèles structuraux ont été proposés en fonction de la composition vitreuse.

Dans le Chapitre II, nous avons étendu nos caractérisations physico-chimiques et structurales aux verres issus du domaine vitreux appartenant au pseudo-ternaire $NaPO_3$ - $Na_2B_4O_7$ - $Ca_5(PO_4)_3OH$.

Un renforcement important de certaines propriétés, notamment la microdureté et la résistance à l'eau, avec l'introduction d'hydroxyapatite a été mis en évidence.

Comme pour les verres issus du pseudo-binaire, les techniques de caractérisation RMN (^{31}P MAS et ^{11}B) et diffusion Raman ont été utilisées pour l'étude structurale. Les résultats obtenus nous ont permis d'établir une corrélation entre les modifications des propriétés physico-chimiques et les changements structuraux et ceci en fonction de la quantité d'hydroxyapatite introduite dans les verres.

La dernière partie de ce travail (Chapitre III) traitera de l'utilisation de nos verres en tant que biomatériaux servant à obturer les caries dentaires. Les matériaux utilisés devaient être fondus, in situ, sous l'action d'un faisceau laser CO_2. Ceux-ci, choisis parmi tous les verres étudiés, devaient satisfaire aux principaux critères spécifiques suivants:

- insolubilité et dureté équivalente à l'émail,
- aptitude à la fusion sous l'impact d'un faisceau laser CO_2 (λ=10,6μm)
- adhésion aux tissus dentaires .

Des essais d'obturation de caries artificielles, débouchant sur un processus de comblement, ont clôturé ce travail .

Cette étude a fait l'objet de trois communications :

- l'une au Deuxième Colloque sur "Les applications des lasers dans les domaines médicaux, industriels et des télécommunications "*Plestin les Grèves, Bretagne*, les 4 et 5 octobre 1990
- l'autre au "5ème REMCES" *Casablanca, Maroc*, les 30-31octobre et 1 novembre 1991
- la dernière aux "Journées de Chimie du Solide", *Montpellier*, les 13 et 14 mai 1993.

CHAPITRE I

VERRES BOROPHOSPHATES DE SODIUM

INTRODUCTION DU CHAPITRE I

C'est en 1962 que K. Tarahashi[1] a mis en évidence un large domaine vitreux dans le ternaire Na_2O-P_2O_5-B_2O_3. L'étude physico-chimique d'un nombre restreint d'échantillons vitreux lui a permis d'avancer que la présence de B_2O_3 conduit à la formation de groupements dits "de type BPO_4" qui serait responsable d'une amélioration substantielle des paramètres étudiés, notamment la résistance à l'eau.

Un peu plus tard, en 1966, P. Beekenkamp et G. E. G. Hardeman[2] ont pu dénombrer, par RMN du ^{11}B, les groupements BO_4 existant dans les verres borophosphatés plutôt riches en formateurs (B_2O_3 et P_2O_5). En s'appuyant sur les résultats obtenus par P. J. Bray et J. G. O'Keefe dans les verres boratés[3], ils ont pu aussi établir des corrélations entre l'évolution de la fraction d'atome de bore en coordinence 4 et certaines propriétés physico-chimiques telles que la résistance chimique et la température de transition vitreuse.

Depuis, seuls des verres borophosphatés au lithium et à l'argent ayant un certain intérêt pour leurs propriétés de conduction ionique ont été caractérisés par diffusion Raman[4, 5] et RMN du ^{31}P[6].

Par contre, les verres issus de l'association $NaPO_3$ - $Na_2B_4O_7$ (composés connus pour leur fort pouvoir vitrifiant mais possédant des propriétés médiocres) n'avaient jamais fait l'objet d'études approfondies. Il semblait donc indispensable de caractériser ces verres dans le domaine de composition (1-x) $NaPO_3$ - x $Na_2B_4O_7$ avant d'ajouter l'hydroxyapatite.

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[1] K. Tarahashi, in "*Advances in glass technology*" Plenum Press, New York, 366,(1962).

[2] P. Beekenkamp et G. E. G. Hardeman, *Verres et Réfr.*, 20, (6), 419, (1966).

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A - CARACTERISATIONS PHYSICO-CHIMIQUES

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PHYSICAL AND CHEMICAL CHARACTERIZATIONS OF SODIUM BOROPHOSPHATE GLASSES.

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Abstract.

The effect of equimolar substitution of sodium metaphosphate by sodium borate on the glass transition (T_g) *and crystallization* (T_c) *temperatures, molar volume* (V)*, density* (ρ)*, microhardness* (H_v)*, solubility in water* (S) *and ultra violet edge absorption* (λ_c) *is studied in the compositional range* $NaPO_3$ - $Na_2B_4O_7$. *An unexpected evolution is observed in the phosphate rich domain implying the presence of* BO_4 *units in the glass.*

1-INTRODUCTION

The interest in borophosphate glasses ensues from the good ability of two glass formers :B_2O_3 and P_2O_5, with various associations of many oxides (alkaline, alkaline-earth, Ag_2O...). Among the numerous previous investigations of borophosphate glasses, we may cite, for instance the study of the ionic conductivity of Ag^+ -containing samples [1] or the structural characterization of Li, K and Ag borophosphate glasses using various techniques (Raman diffusion, NMR...) [2-6]. Sodium borophosphate glasses have been investigated but essentially for low sodium concentration [7].

This work is devoted to the preparation and to the physical and chemical characterizations of sodium-rich glassy samples, namely in the compositional range $NaPO_3$-$Na_2B_4O_7$.

2-EXPERIMENTAL

2-1-Preparation

The vitreous samples present the following chemical composition: (1-x) $NaPO_3$ + x $Na_2B_4O_7$. They are stemmed from the vitreous domain of the Na_2O-B_2O_3-P_2O_5 ternary system detected by K. Takahashi [8], (Figure 1).

Dehydrated $NaPO_3$ and $Na_2B_4O_7$ commercial compounds (purity >99.5%) have been used. The finely ground mixture, put inside a vitreous carbon crucible, was heated using a HF furnace above the melting temperature (700-900°C) in argon atmosphere for 10 to 15 mn. All samples were quenched by switching off the heating system. The resulting weigth losses are lower than 1%.

2-2-Characterizations

2-2-1-Glass transition (T_g) and crystallization (T_c) temperatures

These data have been accurately determined (deviation <5°C) with a DTA Setaram apparatus. The measurements were performed on glass powders introduced in platinum tubes. The heating rate was 350°C. h^{-1} in the 30-900°C range.

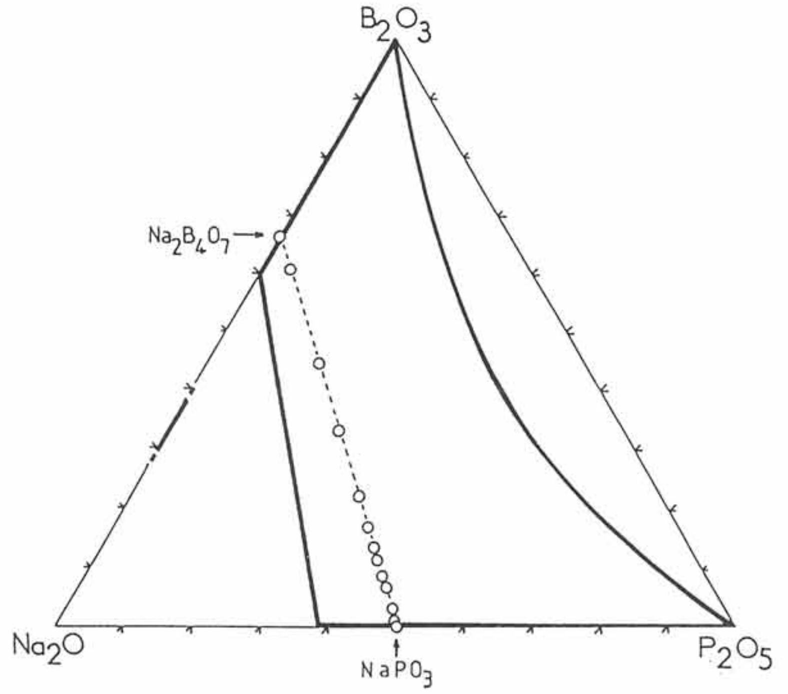

Figure 1-Vitreous domain in the Na_2O-B_2O_3-P_2O_5 ternary system (enclosed in solid line). Glass sample composition (small circle) in the $NaPO_3$-$Na_2B_4O_7$ range (broken line).

2-2-2-Molar volume (V) and density (ρ)

V values are derived from the density measurements (ρ), determined using the hydrostatic pressure concept by immersing the samples in diethyl orthophthalate. The uncertainty of the measurements is estimated to be ±0.01. g. cm^{-3}.

2-2-3-Microhardness (H_v)

The measurements have been made in the Vickers scale of hardness with a Leitz apparatus. The visualization of the pyramidal stamp has been improved by using a gold coating deposition (~50Å) on the polished surface of the glass sample. The accuracy is ± 10 daN. mm^{-2}.

2-2-4-Solubility in water (S)

Samples with parallelepiped shape have been immersed for 1 hour into water (pH=6) at 25°C. The solubility measured in g. cm^{-2}. mn^{-1} was then evaluated by weighing (after carefull drying) the undissolved remaining pieces.

2-2-5-UV edge absorption (λ_c)

The glass samples were cut so as to get parallel polished faces. The absorption spectra were recorded at room temperature with a double - beam Varian Cary 2415 spectrometer.

3-RESULTS

Figures 2-6 respectively show the evolution of the glass transition (T_g) and crystallization (T_c) temperatures, molar volume (V), density (ρ), microhardness (H_v), solubility in water (S) and cut-off wavelength (λ_c) with the absorption coefficient $\alpha = 10$ cm^{-1}, as a function of the B/B+P ratio corresponding to the (1-x) $NaPO_3$ + x $Na_2B_4O_7$ vitreous compositions. We have to point out that the λ_c values, deduced from optical density curves, obey the URBACK relation (exponential form). This latter is characteristic of the glass intrinsic absorption, but not of that resulting from the presence of impurities.

The abovementioned parameters depend on the glass composition as follows:

(i)-T_g (Figure 2) and H_v (Figure 4) have similar evolution, they increase almost linearly with x for B/B+P< 0.5 (x<0.2) and B/B+P>0.6 (x>0.3) and an unhooking occurs between 0.2<x<0.3.

(ii)-T_c (Figure 2) is undetectable for the phosphate - rich and phosphate - poor compositions.

(iii)-V (Figure 3) linearly increases with x for B/B+P<0.5, 0.5<B/B+P< 0.8 and B/B+P>0.8 (i.e. on the whole range of the glass domain) with three distinct slopes. The ρ value reaches a maximum around B/B+P=0.35 and then rapidly falls down.

(iv)-S (Figure 5) and λ_c (Figure 6) abruptly decrease as x increases for small borate compositions (low x values).For the highest borate contents, S exhibits a minimum then a maximum around B/B+P=0.25 and 0.70 respectively , while λ_c reaches a plateau for the intermediate composition and finally increases.

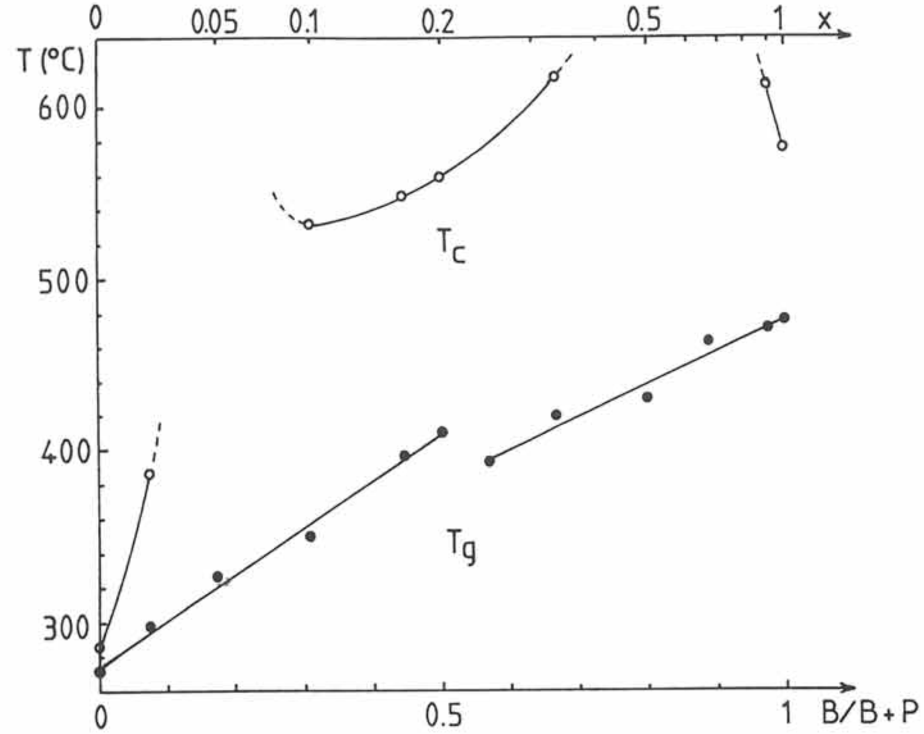

Figure 2-Variation of the glass transition (T_g) and crystallization (T_c) temperatures versus the B/B+P ratio of the (1-x) $NaPO_3$ + x $Na_2B_4O_7$ glass sample composition.

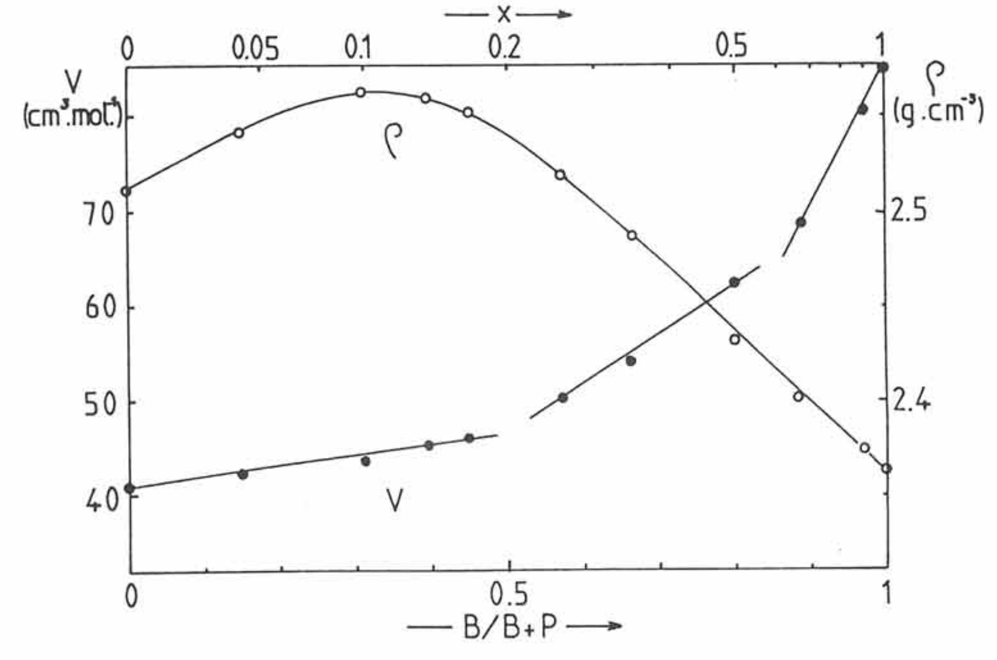

Figure 3-Variation of the molar volume (V) and density (ρ) versus the B/B+P ratio of the (1-x) $NaPO_3$ + x $Na_2B_4O_7$ glass sample composition.

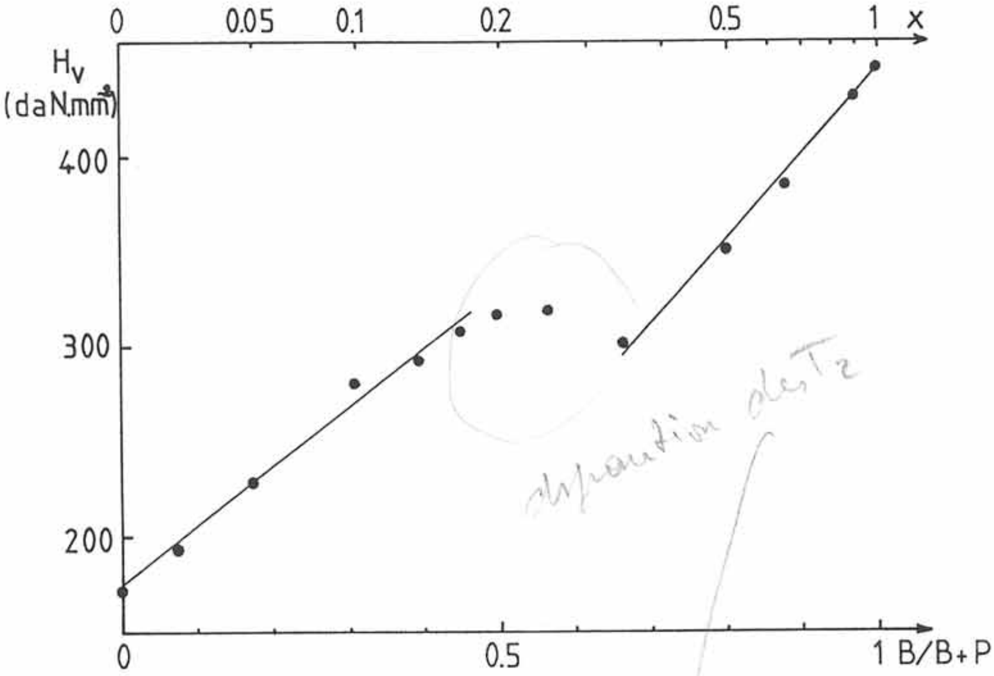

Figure 4-Variation of the microhardness (H_V) versus the B/B+P ratio of the (1-x) $NaPO_3$ + x $Na_2B_4O_7$ glass sample composition.

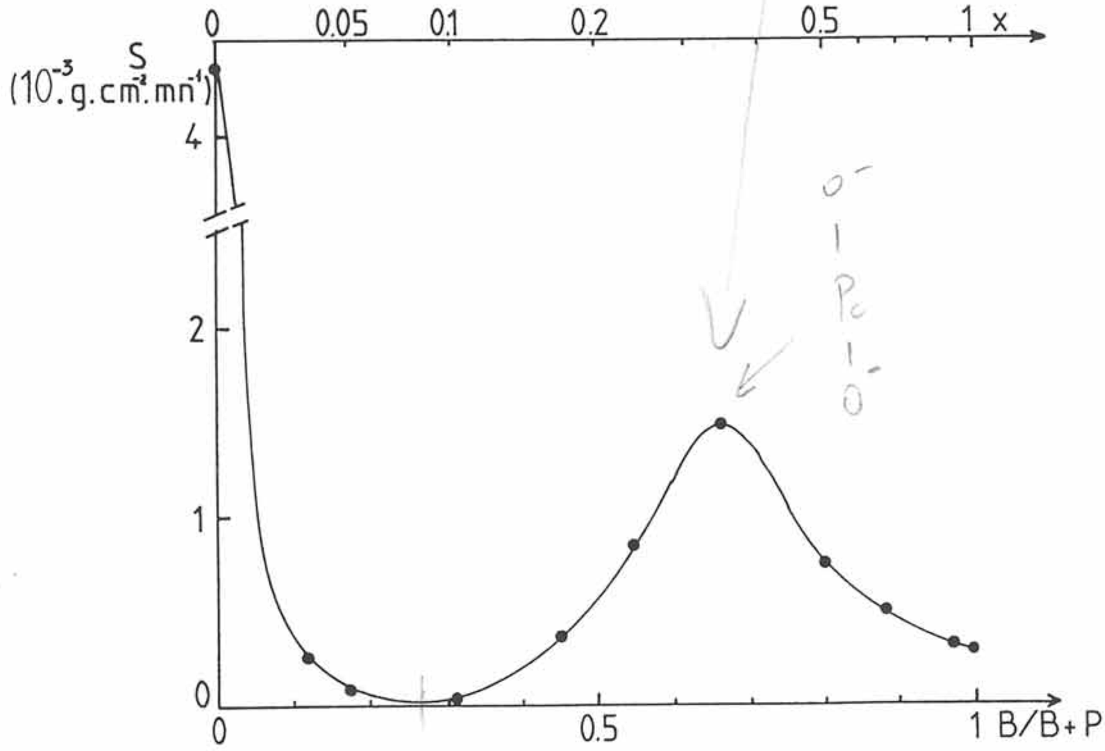

Figure 5-Variation of the solubility (T=25°C; pH=6) in water (S) versus the B/B+P ratio of the (1-x) $NaPO_3$ + x $Na_2B_4O_7$ glass sample composition.

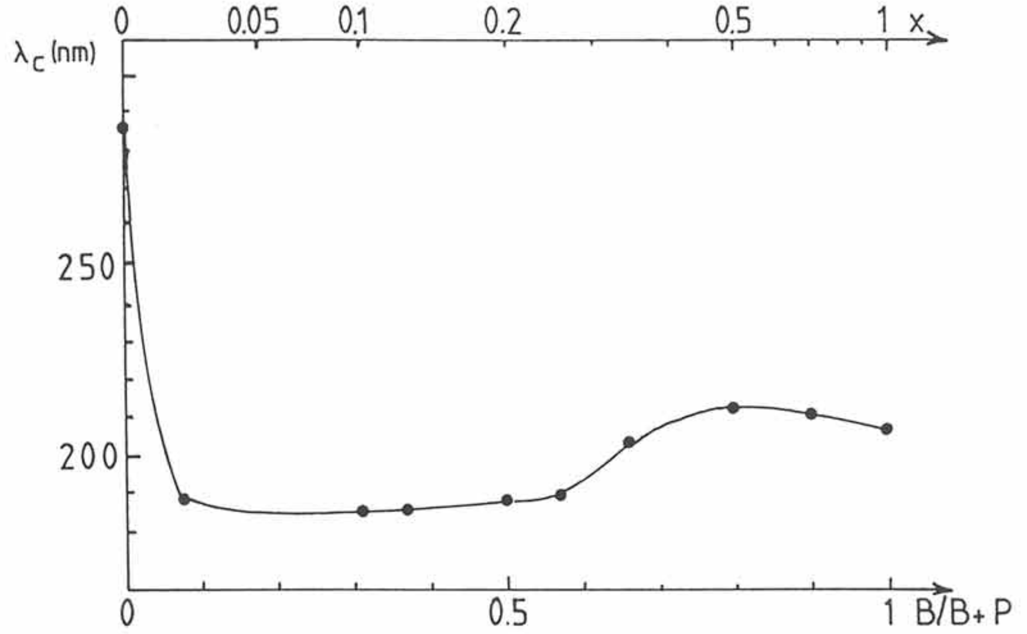

Figure 6-Variation of the cut - off wavelength (λ_c) in UV domain with the absorption coefficient $\alpha = 10\ cm^{-1}$ versus B/B+P ratio of the (1-x) $NaPO_3$ + x $Na_2B_4O_7$ glass sample composition.

4-DISCUSSION

It is noteworthy to remark that small amounts of $Na_2B_40_7$ introduced into the $NaPO_3$- based samples induce significant modifications of their physical and chemical properties.A deep structural change seems to account for these modifications.

The borate addition involves a strong decrease of the Na/B+P ratio in the glass, and therefore an increase in the glass - former content, probably associated with a strengthening of the glass network.

Previous studies [2, 7] have shown that boron atoms form BO_3 and BO_4 units within the glass network. The rate of tetrahedral boron motifs reaches 78% for the 0.875 $LiPO_3$ + 0.125 $Li_2B_4O_7$ glass composition [5] and is close to 50% for $Li_2B_4O_7$ or $Na_2B_4O_7$ glasses

[9]. The excess of the negative charge on the BO_4 unit is compensated either by the charge of the modifier cation or by the excess of the positive charge on the PO_4 unit.

Therefore B-O-P bridge formation should occur in the phosphate - rich domain and account for the observed modification of the properties studied . Whithin this compositional range, the structural considerations may be the following:

(i)-the rise of T_c results from an increasing disorder of the glass network.

(ii)-according to the Stevels theory [10], the drop of λ_c corresponds to the reduction of the non - bridging oxygen atoms. Similar behaviour has been observed in the phosphate [11], borate and borosilicate glasses [12, 13]. The consequence is the random ramification of the glass network, associated with the better compactness, as illustrated in Figures 3-5.

The anomalous behaviour of some properties such as T_g and H_v close to B/B+P=0.5 (x=0.2) would result from a structural change of the glass network with probably the crossing from a ramified borophosphate to a borate network. In this latter, the presence of phosphorus atoms induces, here again, a strong disorder of the structure (T_c undetectable) with a weakening of this glass network (λ_c and S increasing).

5-CONCLUSIONS

The physical and chemical characterizations of glasses having the composition (1-x) $NaPO_3$ + x $Na_2B_4O_7$, give evidence of an anomalous evolution of studied properties such as glass transition (T_g) and crystallization (T_c) temperatures, molar volume (V), density (ρ), microhardness (H_v), solubility in water (S) and cut off wavelength in the UV region (λ_c).

From low to high borate content, T_g and H_v increase discontinuously in the intermediate compositional domain. V increases slowly in the borate - poor domain and more steeply for x>0.2. S and λ_c immediatly fall down as soon as small amounts of borate atoms are introduced, then weakly increase for high borate concentrations. T_c rises within the whole compositional domain but is undetectable in the $0.02<x<0.10$ and $0.33<x<0.90$ compositional ranges.

The following structural considerations can be argued:

(i) for glasses containing small amounts of $Na_2B_4O_7$, the presence of BO_4 tetrahedral, associated with the B-O-P bridge formation, induces a random ramification and the compactness of the borophosphate glass network.

(ii) for higher concentration of $Na_2B_4O_7$, the diborate structure gradually substitutes for the rigid borophosphate network.

These structural hypotheses are now confirmed by use of NMR and Raman techniques and will be presented elsewhere for the sake of clarity.

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B - CARACTERISATIONS STRUCTURALES

B-1-ETUDE PAR RMN DU ^{31}P (MAS) ET DU ^{11}B

Nous venons de mettre en évidence un comportement inattendu de l'ensemble des caractéristiques physico-chimiques étudiées dans le système vitreux (1-x) $NaPO_3$ x $Na_2B_4O_7$.

De ces évolutions, deux considérations structurales peuvent être formulées:

i) d'une part, la modification importante de certaines propriétés (densité, microdureté, insolubilité...) dès l'introduction de bore pourrait être due à la présence de tétraèdres BO_4 contribuant à la formation d'un réseau borophosphaté ramifié

ii) d'autre part, pour x voisin de 0,2, on observe une discontinuité dans les propriétés étudiées (température de transition vitreuse, microdureté, volume molaire...) traduisant une modification importante de la structure; celle-ci pouvant résulter de la formation de cycles, comme dans $Na_2B_4O_7$.

Des études RMN ont été entreprises afin d'obtenir des informations sur le proche environnement des atomes de bore et de phosphore.

- La RMN du ^{11}B permettant de dénombrer les atomes de bore tétra et tricoordinés, appartenant respectivement à des unités BO_4 et BO_3.

- La RMN MAS (Magic Angle Spinning) du ^{31}P permettant, quant à elle, de dénombrer les différents types d'unités phosphatées existant dans ces verres.

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^{31}P MAS (MAGIC ANGLE SPINNING) AND ^{11}B NMR STUDY OF SODIUM-RICH BOROPHOSPHATE GLASSES.

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Abstract.

^{31}P MAS and ^{11}B NMR have been used for structural investigations on the glass samples with chemical composition (1-x) $NaPO_3$ - x $Na_2B_4O_7$. The ^{31}P resonance spectra present several Gaussian lines which are due to different types of environment of PO_4 units. In addition to the phosphate units occuring for $R \geq 1$ in the R Na_2O-P_2O_5 system (i.e. middle: MP, end: EP and monomeric: MO units), typical phosphate units included into borophosphate groups have been identified in MAS spectra. From ^{11}B spectra, the boron atom fraction in four-fold coordination has been determined. The addition of $Na_2B_4O_7$ progressively produces a shortening of the length of phosphate chains. The borate groups, mainly under the $BO_{4/2}^-$ form compensated by phosphate units, are used as branching units between chains, with probably a tendency of random ramification with phosphate groups, resulting in the formation of borophosphate groups of the form: $BOPO_2^{2-}OP$ and $BOPO_2^-OP$ (MB_1) then $BOPO_2^{2-}OB$ and $BOPO_2^-OB$ (MB_2), as x increases up to 0.2. In the borate rich concentration range ($0.20<x\leq1$), borate groups including boron atoms in three- and four-fold coordination such as those found in pure vitreous $Na_2B_4O_7$, would be considered. The phosphate units bridging the borate groups (MB_2) are located out of the borate network and progressively disappear giving place to $BOPO_3^{2-}$ (EB) and MO units as x increases.

1-INTRODUCTION

In a recent paper sodium-rich borophosphate glassy samples have been prepared, namely in the compositional range $NaPO_3$-$Na_2B_4O_7$. The physical and chemical properties such as, glass transition (Tg) and crystallization (Tc) temperatures, molar volume (V), microhardness (Hv), solubility in water (S) and cut off wavelength in the UV region (λ_c) have been measured [1].

Nuclear Magnetic Resonance (NMR) is a useful technique to investigate the short range order and particularly to provide information about coordination and bonding of resonating species.

With the help of the Magic Angle Spinning (MAS) NMR technique, M. Villa et al [2] and F. Tian et al [3] recently showed changes in bonding and environment of PO_4 units in lithium borophosphate glasses, because the isotropic ^{31}P chemical shift for each phosphate species occurs in well-separated spectral region. More recently, several authors have shown that similar information can be obtained for other alkali phosphate glasses [4, 5].

On the other hand, ^{11}B NMR has been applied to the study of structure and chemical bonding of alkali borate [6, 7], borosilicate [8], boroaluminate [9] and alkali borophosphate [3, 10] glasses. In particular, NMR has been used to determine the fraction of boron atoms in BO_4 and BO_3 units.

This paper is devoted to the structural investigation of a series of glasses with compositions (1-x) $NaPO_3$ - x $Na_2B_4O_7$ using ^{31}P MAS and ^{11}B NMR spectroscopies. The ^{31}P chemical shifts will be related to changes in bonding and environment of the PO_4 units in conjonction with the analysis of the profile evolution of ^{11}B NMR line (determination of BO_4 unit fraction) as a function of the glassy composition. Finally, structural interpretations will be suggested and correlated with the physical and chemical properties [1].

2-EXPERIMENTAL DETAILS

2-1-Preparation

The glass samples studied in this work have been prepared as described previously [1]. They stem from the vitreous domain of the Na_2O-P_2O_5-B_2O_3 ternary system with $\frac{1+x}{2(1+2x)}$ Na_2O + $\frac{1-x}{2(1+2x)}$ P_2O_5 + $\frac{4x}{2(1+2x)}$ B_2O_3 equivalent composition in Figure 1. Their compositions (x values) and B/B+P corresponding ratios are reported in Table 1.

N°	x	B/B+P
1	0	0
2	0.02	0.075
3	0.05	0.167
4	0.10	0.308
5	0.13	0.374
6	0.17	0.444
7	0.20	0.500
8	0.25	0.571
9	0.33	0.667
10	0.50	0.800
11	0.67	0.889
12	0.91	0.968
13	1.00	1.000

Table 1- Composition (1-x) $NaPO_3$ - x $Na_2B_4O_7$ and $\frac{B}{B+P}$ ratio value corresponding to the glass samples studied by ^{31}P MAS and ^{11}B NMR.

Moreover, five additional samples in the Na_2O rich part of the Na_2O-B_2O_3 binary system were prepared by mixing Na_2CO_3 and B_2O_3 starting commercial compounds (purity >99.5%) to determine the BO_4 units fraction. The compositions are listed in Table 2.

The crystalline Na_3PO_4, $Na_4P_2O_7$ and $Na_5P_3O_{10}$ have been prepared by heating adequate mixture of $NaPO_3$ and Na_2CO_3 commercial compounds (purity >99.5%) at 900°C then, recrystallized at 500°C during several hours.

y	0.333	0.375	0.400	0.620	0.667	0.706
R=y/1-y	0.500	0.600	0.667	1.632	2.000	2.400

Table 2- Glass composition $yNa_2O+(1-y)B_2O_3$ of samples studied by ^{11}B NMR.

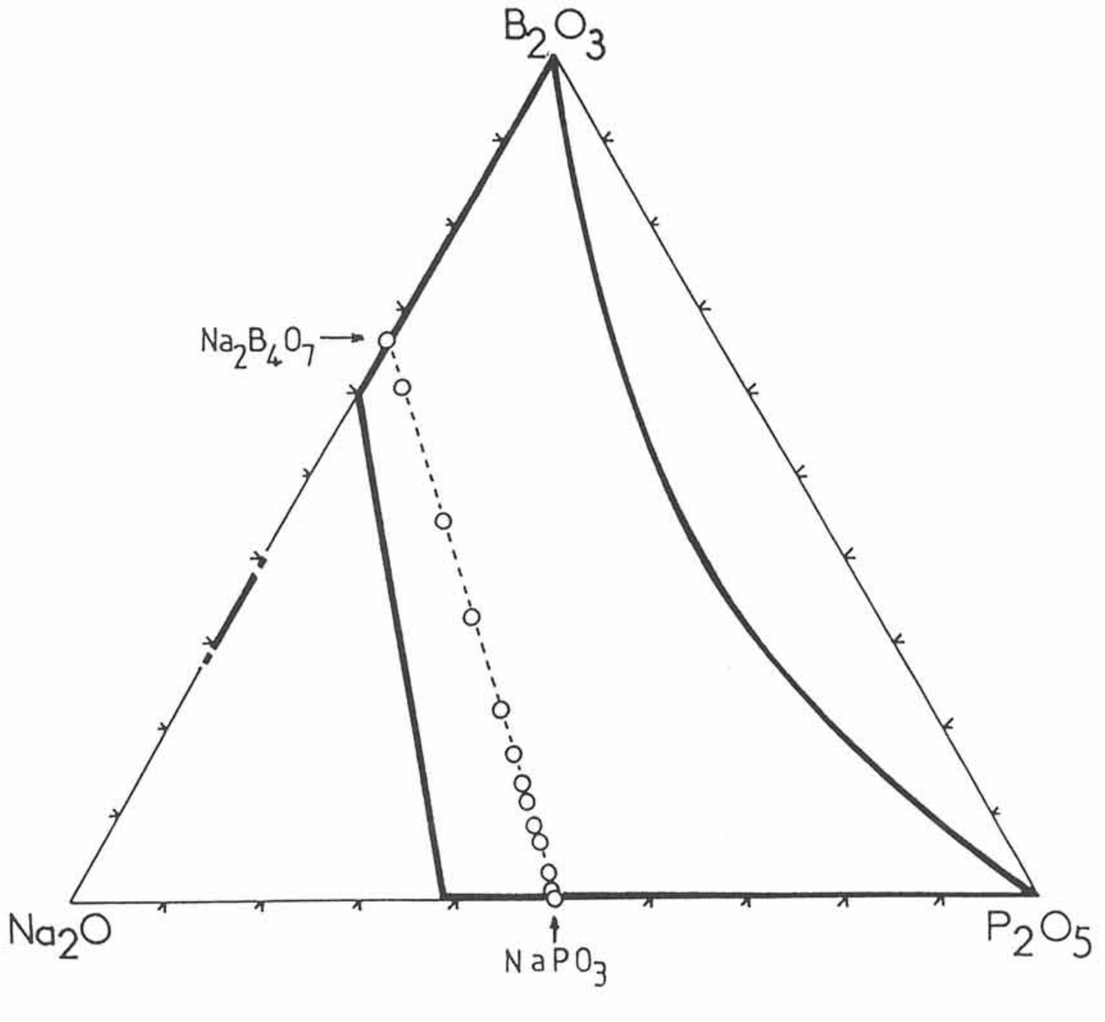

Figure 1- Vitreous domain (solid line) and glass samples (small circle) studied by NMR.

2-2-NMR

^{31}P and ^{11}B NMR spectra were recorded on a high power BRUKER MSL 200 spectrometer equipped with a 4.7 T superconducting magnet.

The single pulse sequence (Px-τ-acquisition) was used for MAS experiments because of long T_1's and compared to cyclops sequence (90°x-τ-acquisition). The shifts of the lines were referenced to 85% phosphoric acid measured in the same probe. The spectrometer operating conditions were as follows:

- -spectrometer frequency: 80.962 MHz
- -pulse program: onepulse and cyclops
    - -pulse-width: 1 μs for onepulse and 3 μs for cyclops
    - -dead time delay: 20 μs
    - -recycle delay time: 60 s
    - -spinning speeds: 4 KHz and 5 KHz
- -spectral width: 125 KHz

The simulation of the ^{31}P NMR lines were performed using the "Linesim" program delivered by BRUKER. This program allows to adjust peak positions, peak heights, line widths, ratios of Gaussian and Lorentzian function and relative proportions of their areas.

^{11}B NMR spectra were recorded using a solid echo sequence (90°x-τ-90°y-τ'-acquisition) with 8 phase cycling. The spectrometer operating conditions were as follows:

- -spectrometer frequency: 64.168 MHz
- -pulse program:
    - -90° pulse length: 3 μs
    - -recycle time: 60 s
- -spectral width: 500 KHz

3-RESULTS AND INTERPRETATION

3-1-^{31}P MAS NMR

Before the analysis and interpretation of ^{31}P MAS NMR spectra, reported in Figures 2-4, we propose to define the main different phosphate units that it is possible to find in the borophosphate glasses, according to Villa's work [2]:

-*branching units:* $O_{3/2}P{=}O$ *(BP)*, bonded to three phosphorus atoms, as in crystalline P_2O_5

-*borophosphate units:* $PO_{4/2}^{+}$ bonded to four boron atoms in four-fold coordination ($BO_{4/2}^{-}$), designed as *BB*, found in crystalline BPO_4

-*middle units:* $O_2PO_{2/2}^{-}$ bonded to two phosphorus (*MP*), as in metaphosphate compounds, or one phosphorus and one boron atoms (*MB_1*) or two boron atoms (*MB_2*)

-*end units:* $O_3PO_{1/2}^{2-}$ may be bonded to one phosphorus atom (*EP*) or one boron atom (*EB*)

-*monomer unit:* PO_4^{3-} (*MO*).

The structural formulas and symbols of these phosphate units are reported in Table 3.

Name	Symbol	Structure
Branching	BP	$O{=}\mathbf{P}O_3P_3$
	BB	$\mathbf{P}O_4B_4$
Middle	MP	$PO\mathbf{P}O_2^{-}OP$
	MB_1	$PO\mathbf{P}O_2^{-}OB$
	MB_2	$BO\mathbf{P}O_2^{-}OB$
End	EP	$PO\mathbf{P}O_3^{2-}$
	EB	$BO\mathbf{P}O_3^{2-}$
Monomer	MO	$\mathbf{P}O_4^{3-}$

Table 3- Structural formulas and symbols of phosphate units in borophosphate glasses. (**P**: considered phosphorus).

For comparison, ^{31}P MAS NMR of crystalline $Na_5P_3O_{10}$, $Na_4P_2O_7$, Na_3PO_4 and BPO_4 have been studied. The resonance lines have been assigned by structural analogy. The

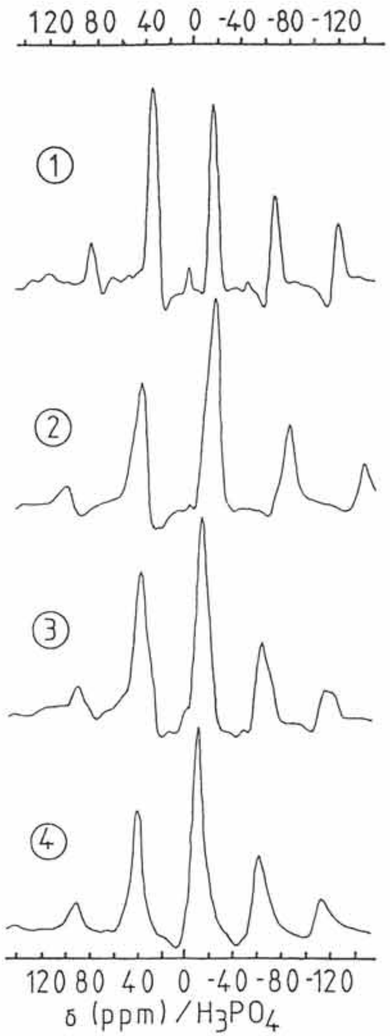

Figure 2- ^{31}P MAS NMR spectra (4 KHz) of glasses 1-4.

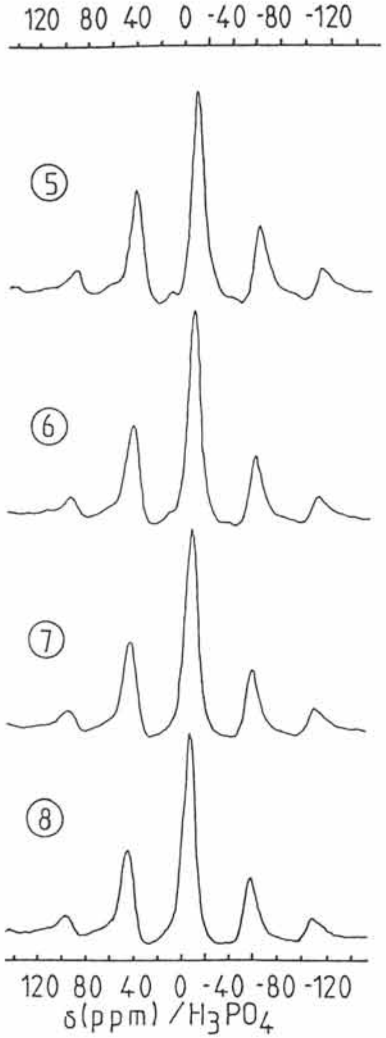

Figure 3- ^{31}P MAS NMR spectra (4 KHz) of glasses 5-8.

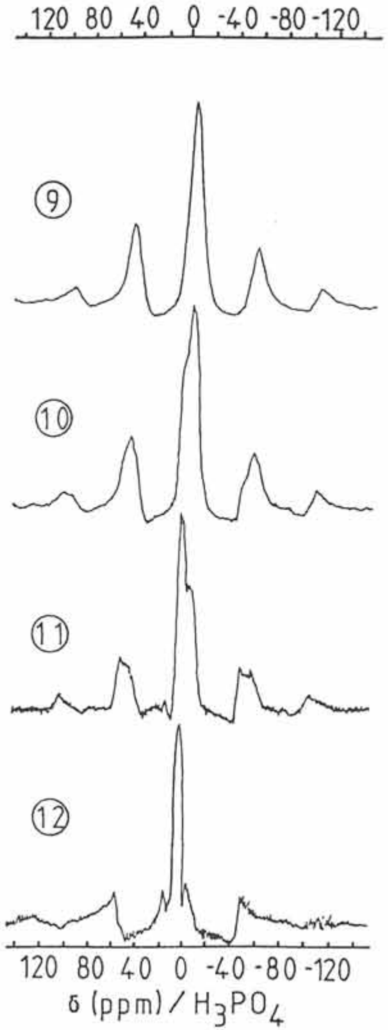

Figure 4- ^{31}P MAS NMR spectra (4 KHz) of glasses 9-12.

isotropic chemical shifts (δ ppm) found are in agreement with those reported in literature [2, 11-14] and are listed in Table 4.

Compound	Unit type	Isotopic Chemical Shift (ppm/H_3PO_4)	
		This work	Literature
$Na_7P_5O_{16}$	MP		-16.6 [11]
	EP		+1.0 [11]
$Na_5P_3O_{10}$	MP	-8.9	-8.0 [12]
	EP	-0.2	+1.2 [12]
$Na_4P_2O_7$	EP	+1.3	+1.6 [13]
Na_3PO_4	MO	+14.1	+14.0 [14]
BPO_4	BB	-31.2	-30.0 [2]

Table 4- ^{31}P NMR isotropic chemical shifts of crystalline BPO_4 and some phosphates with different degree of polymerization.

The observed ^{31}P MAS NMR lines have been labelled (a), (b).... They are represented schematically in Figure 5, together with the position range of the isotropic chemical shifts of each phosphate unit, defined in Table 3, found in Li and Ag borophosphate glasses [2] and crystalline phosphates (Table 4). Figure 6 shows the evolution of isotropic chemical shift of these various lines as a function of x. These two figures will be used as references for the following study.

3-1-1-Sodium metaphosphate glass

The spectrum is mainly dominated by two lines (a, c). The more intense (line a) with δ=-20ppm is assigned to MP units. The line (c) (δ=2ppm) with peak area ten times smaller than line (a) corresponds to EP units. This interpretation is in excellent agreement with R. K. Brow et al's ^{31}P MAS NMR study of sodium phosphate glasses [4]. The area ratio of these two lines permit to evaluate that the average length of phosphate chains is close to twenty phosphorus.

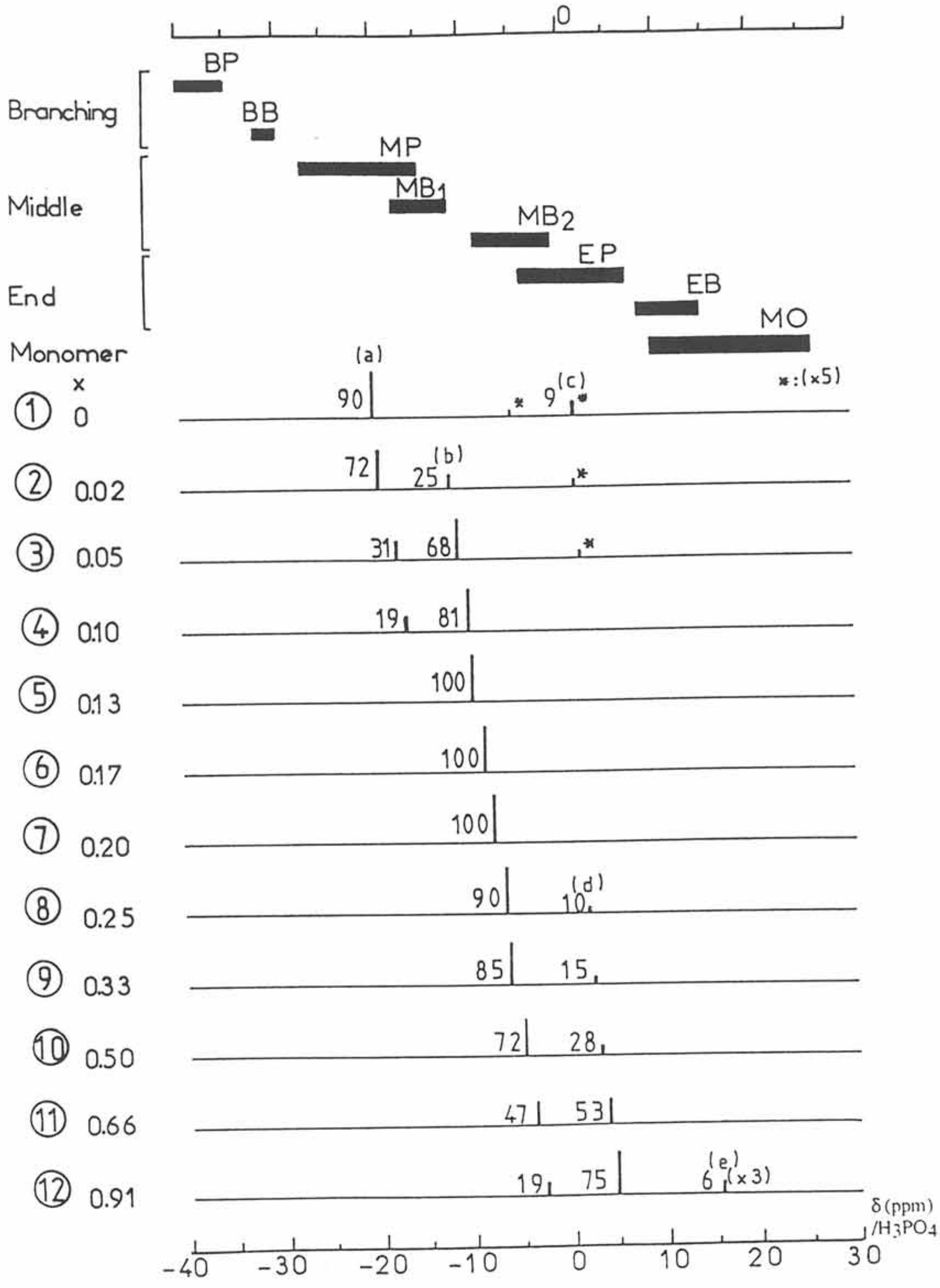

Figure 5-Schematic representation of observed ^{31}P MAS NMR (Figures. 2- 4) spectra of borophosphate glasses together with position domains of the isotropic chemical shifts of various phosphate units (Table 3) corresponding to the crystalline phosphates, borophosphates and Li-, Ag- borophosphate glasses [2].The numeric value characterizes the area percentage corresponding to the a, b, c, d and e peaks respectively assigned to P atom in MP, MB_1 then MB_2, EP, EB and MO units. (*) peak intensity × 5.

The presence of the small line at δ=-5ppm might be assigned to H^+-bonded EP, as suggested by M. Villa et al in Graham's salt [15].

3-1-2-Sodium borophosphate glasses

The evolution of ^{31}P MAS NMR spectra can be divided in three separate compositional regions.

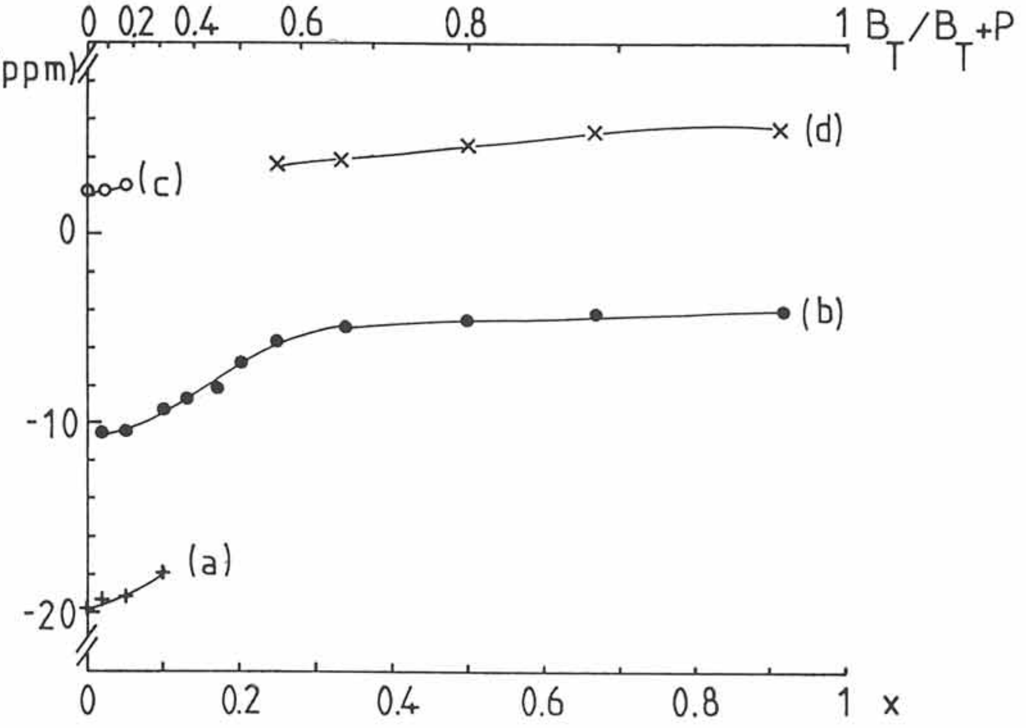

Figure 6-Evolution of the isotropic chemical shifts of the main ^{31}P MAS NMR lines (a-d) as a function of x.

At the first addition of $Na_2B_4O_7$, we notice , the positive δ shift and the intensity decrease of the line (a) up to x=0.10 (Figure 6), the progressive disappearance of line (c) and the appearance of a new resonance peak (line (b)), with δ=-11ppm, corresponding probably to the MB_1 units. The δ shift suggests modifications in the charge distribution in phosphorus-non-bonding oxygen bonds (i.e. a decrease of the π character of the P=O bond with a delocalization of the electron on the three other P-O bonds mainly due to a shortening of chain phosphate length [14]).

From x>0.10, only one peak which rapidly shifts from δ=-10ppm to δ=-6ppm for x=0.25, is observed (Figure 6). This chemical shift position is located between these of MB_1 and MB_2 units. It may be tempting to assign this behaviour to the progressive conversion of MB_1 to MB_2 units.

For x= 0.25, a new signal (line d) appears in the chemical shift region of EP units. We rule out that this peak is due to the resonance of these units because the composition of this glass is richer in boron atoms than in phosphorus atoms, consequently the probability to find $O_{1/2}PO_3^{2-}$ units bridging another phosphorus atom is very weak. Hence, we are tempted to identify it with the EB units. When increasing the borate fraction, the intensity of line (d) rapidly increases while that of line (b) decreases together with a weak shift in both cases. At x=0.91, the ^{31}P MAS NMR spectrum presents a main peak around δ=5ppm (EB units) and two smaller peaks at δ=-3ppm (MB_2 units) and δ=15ppm (line (e)). The chemical shift of this last line is close to those observed for crystalline Na_3PO_4 (δ=14ppm). We assign it to the MO units.

3-2-^{11}B NMR

The ^{11}B NMR spectra of some vitreous samples are shown in Figure 7. The evolution of these spectra exhibits an evident environment change of boron atoms in these glasses.

As the matter of fact, we recall that the ^{11}B atom, with a nuclear spin equal to 3/2, has an electrical quadrupole moment which can strongly interact with the electric field gradient appearing while the boron environment deviates from the cubic symmetry. So, the boron atoms in four- and three-fold coordinations (respectively called B_{IV} and B_{III} subsquently in the text) present two different signals. Like this, the central narrow peak is due to B_{IV} atoms, in an environment rather symetrical, which only display a weak first order nuclear quadrupole interaction. The second order quadrupole interaction generates a broad resonance produced by the electric field gradient at the site of the B_{III} atoms in trigonal planar coordination. For more details see ref. [16].

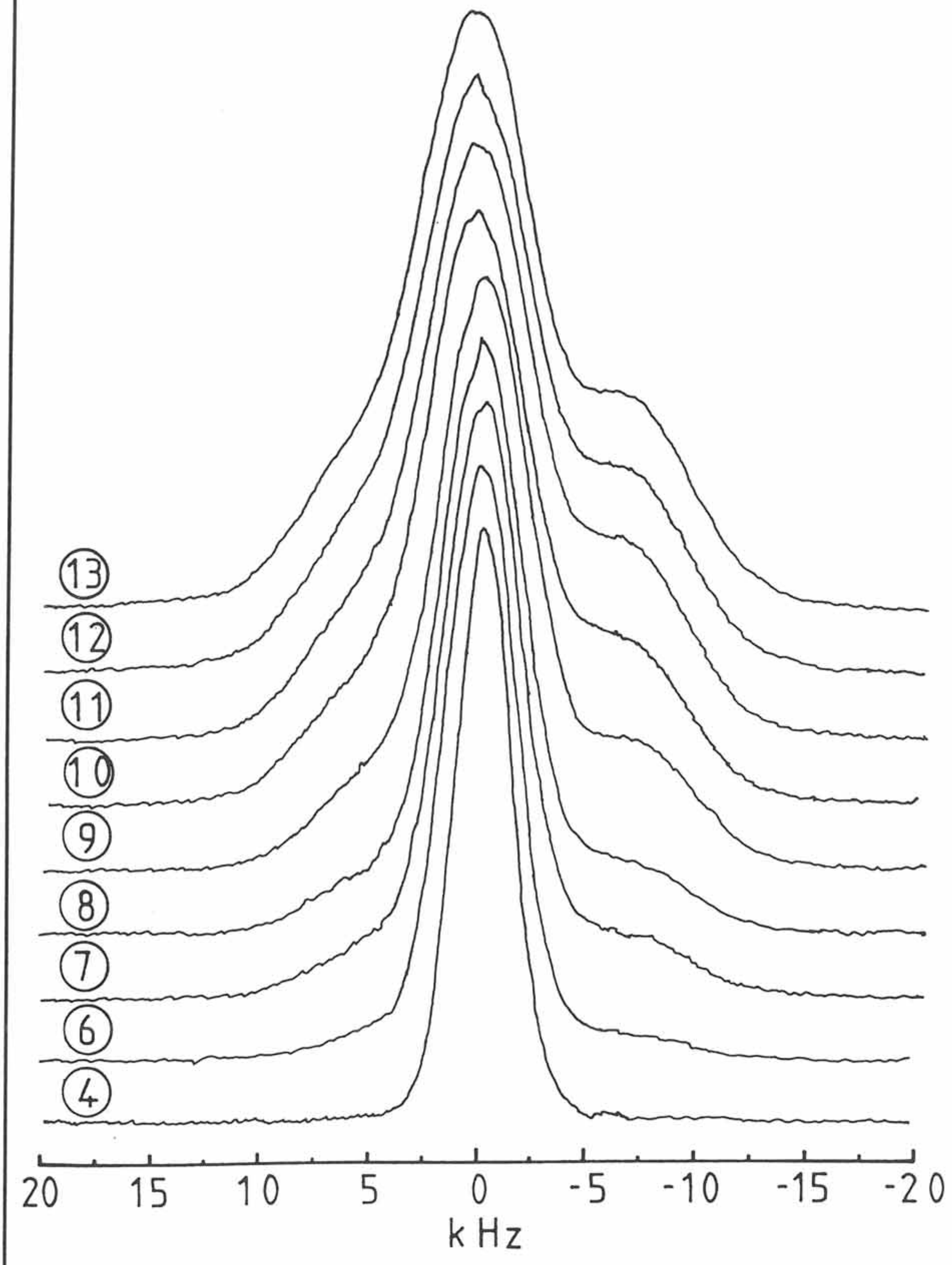

Figure 7-^{11}B NMR spectra of some vitreous samples.

In Figure 7, the spectra successively show the presence of B_{IV} atoms mainly for weak x values and the two environment types (B_{III} and B_{IV} atoms) for higher borate concentration. A measurement of the area under the central peak, with respect of the total area under the entire absorption curve, gives the fraction of B_{IV} atoms. Detailed discussion of this procedure has been already published by Y. H. Yun et al [6].

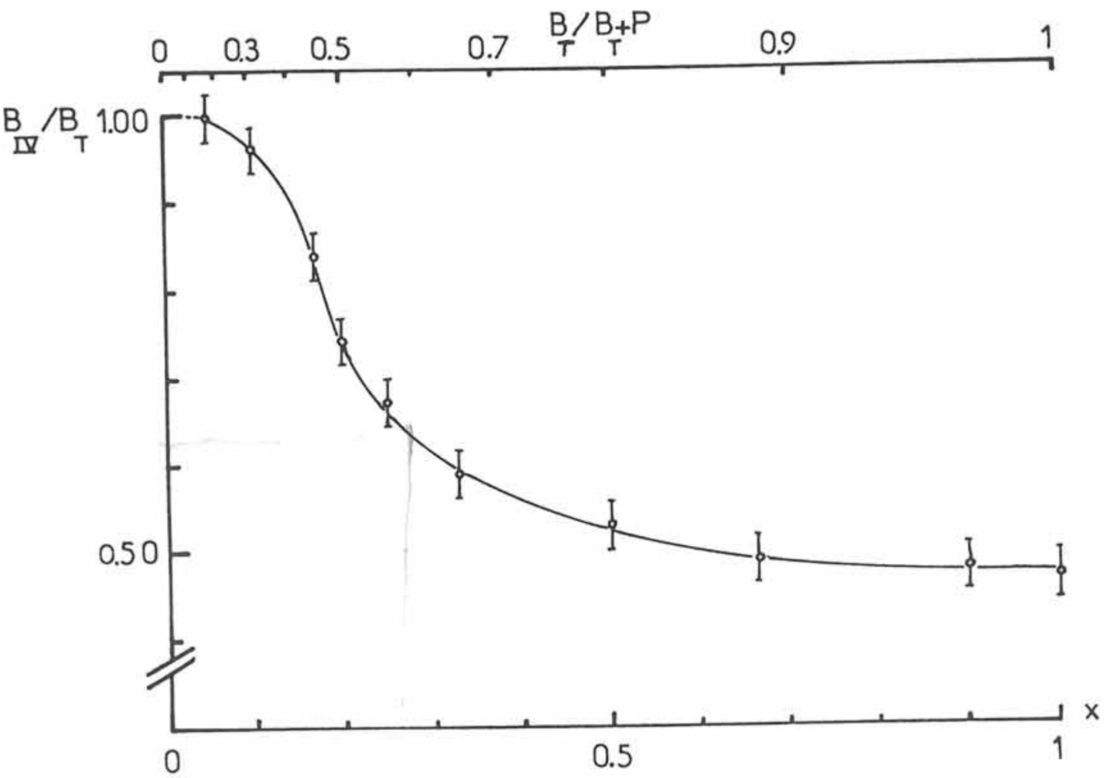

Figure 8- Evolution of B_{IV} atom fraction as a function of x.

The B_{IV} atom fraction in relation to total boron atoms (B_T) has been reported in Figure 8 as a function of x and the B_T/B_T+P ratio. Three regions can be distinguished:

i)- in the rich-phosphate part ($x \leq 0.1$; $B_T/B_T+P \leq 0.3$), the almost totality of boron atoms take place in four-fold coordination,

ii)- from x=0.1, the B_{IV} atom fraction abruptly decreases up to x close to 0.6 ($B_T/B_T+P \approx 0.85$), iii)- in the rich-borate part, the B_{IV} atom fraction slowly tends towards 0.47, corresponding to vitreous $Na_2B_4O_7$.

This value is in agreement with those recently found by several authors [7, 16, 17].

It is generally agreed that the alkali borophosphate glasses can contain the borate units as in alkali borate glasses but also new units. The B_{III} atoms can be surrounded by bridging oxygen atoms (type a) or/and by one non bridging and two bridging oxygen atoms (type b). The B_{IV} atoms surrounded by four bridging oxygen atoms form $B_{IV}O_{4/2}^-$ units , where the excess of negative charge can be compensated either by alkali modifier, forming the C_{Na} unit, or by the excess of positive charge of $P_cO_{4/2}^+$ unit forming $O_{3/2}B_cOP_cO_{3/2}$ unit (type C_P), according to previous studies [18-20].

The number of B_{III} atoms ($N_{B_{III}}$) and B_{IV} atoms ($N_{B_{IV}}$) in relation to the total number of former atoms (B_T+P) can be expressed by the following relations:

$$N_{B_{III}} = (N_{B_{III}})_a + (N_{B_{III}})_b$$

$$N_{B_{IV}} = (N_{B_{IV}})_{Na} + (N_{B_{IV}})_P$$

where $(N_{B_{III}})_a$, $(N_{B_{III}})_b$, $(N_{B_{IV}})_{Na}$ and $(N_{B_{IV}})_P$ are respectively the ratio of the number of the a, b, C_{Na} or C_P units in relation to the total number of the former atoms.

In this work, the types a and b units cannot be distinguished although P. J. Bray et al have observed two different NMR signals [16]. In addition, it is not possible to quantify the two C_{Na} and C_P units from the deconvoluted line of $^{11}B_{IV}$ NMR signal.

An indirect approximative determination of these two B_{IV} forms is to consider the following hypotheses:

i)- in the y Na_2O+(1-y) B_2O_3 compositional glasses, the presence of oxygen excess, introduced by Na_2O, gives rise to formation of C_{Na} and type b units only [21], according to the following equilibrium:

$$\underset{(C_{Na})}{BO_{4/2}^-, Na^+} \leftrightarrow \underset{\text{(type b)}}{O_{2/2}BO^-, Na^+}$$

ii)- in the (1-x) $NaPO_3$ - x $Na_2B_4O_7$ or equivalent

$$\frac{1+x}{2(1+2x)} Na_2O + \frac{1-x}{2(1+2x)} P_2O_5 + \frac{4x}{2(1+2x)} B_2O_3$$

($0 \leq x \leq 1$) glass composition, the oxygen ions, introduced by Na_2O, give rise to formation , not only of C_{Na} and b units as in sodium borate glasses, but also of $O_2PO_{2/2}^-$, Na^+ units as in phosphate glasses with an equilibrium between these three units.

iii)- if we admit that this equilibrium depends mainly on the Na_2O concentration and in addition, the degree of the type b $\leftrightarrow$ C_{Na} equilibrium is the same in the two glass types (not affected by the phosphorus presence), then it is possible to know the fraction of C_{Na} units in the borophosphate glasses from the experimental determination of B_{IV} atoms in the sodium borate glasses at $y \geq 0.33$. By difference, we can deduce the fraction of C_P units.

The evolution of the $(B_{IV})_{Na}$ atom fraction in the borate glasses as a function of $R=y/1+y$ ratio ($y \geq 0.33$) is reported in Figure 9. The value of $(B_{IV})_{Na}$ fraction reaches a maximum around R=0.6 and then decreases as R increases. The broken line corresponds to the extrapolation of the non-vitreous part between the two glassy domains (see Figure 1) according to the previous data of Li_2O-B_2O_3 glass system [6].

The transposition of the $(B_{IV})_{Na}$ fraction data for the sodium borate glasses to the borophosphate glasses has permitted to estimate $(N_{B_{IV}})_{Na}$ and $(N_{B_{IV}})_P$ fractions using the following relations:

$$R = \frac{y}{1-y} = \frac{1+x}{1+3x}$$

$$(N_{B_{IV}})_{Na} = (B_{IV})_{Na} \frac{4x}{1+3x}$$

$$\text{and } (N_{B_{IV}})_P = (N_{B_{IV}}) - (N_{B_{IV}})_{Na}$$

The $(N_{B_{IV}})$, $(N_{B_{IV}})_{Na}$ and $(N_{B_{IV}})_P$ variations, as a function of x, are reported in Figure 10. $(N_{B_{IV}})_P$ value reaches a maximum around x=0.2 and rapidly decreases while the value of $(N_{B_{IV}})_{Na}$ is minimum then increases with x. In the $0.6<x\leq 1.0$ compositional range, only C_{Na} units exist in the glasses. The fact that the maximum of the C_P units approximatively corresponds to the vitreous composition with an equal proportion of P and B atoms well

corroborates the procedure used for the $(N_{B_{IV}})_{Na}$ determination and the hypothesis considered above.

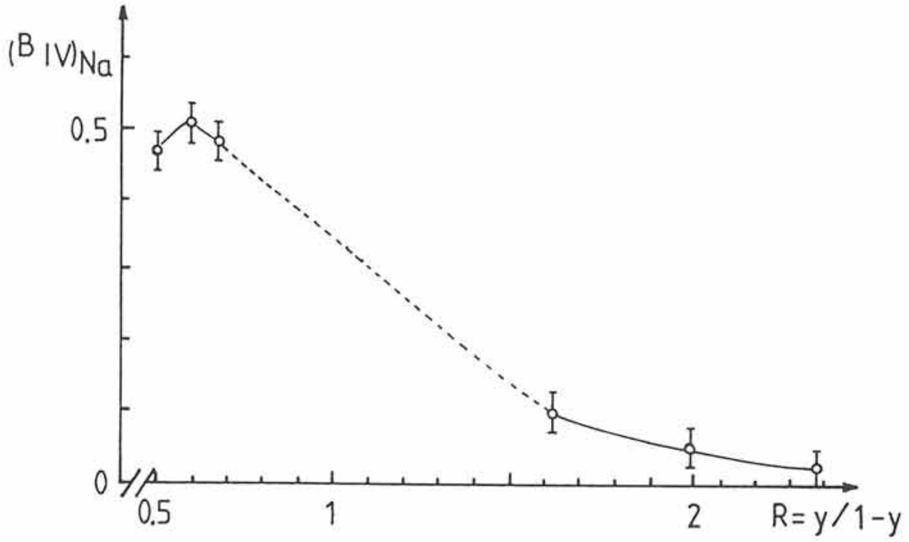

Figure 9-Evolution of $(B_{IV})_{Na}$ atom fraction in y Na_2O+(1-y)B_2O_3 compositional sodium borate glasses as a function of x. The broken line corresponds to the non-vitreous domain.

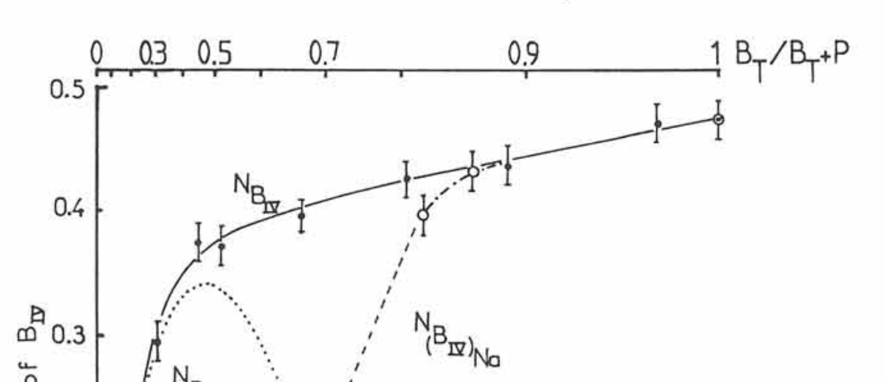

Figure 10-Evolution of $(N_{B_{IV}})$ (solid line), $(N_{B_{IV}})_{Na}$ (broken line) and$(N_{B_{IV}})_P$ (dotted line) atom fractions as a function of x.

As previously mentioned by P. J. Bray et al [16], the variation of the width at half-height of the $^{11}B_{IV}$ resonance line ($\Delta\nu_{B_{IV}}$) also gives information about the evolution of the B_{IV} environment. If we consider that the boron atom is closer to the Na^+ anion in the C_{Na} units than to the phosphorus atom playing the role of charge compensator in C_P units, the pertubation of the symmetry of the electric field gradient will stronger for the boron atom in C_{Na} units than in C_P units. Consequently, the $\Delta\nu_{B_{IV}}$ increase will be correlated to the increase of C_{Na} unit number. In Figure 11, the $\Delta\nu_{B_{IV}}$ evolution agrees with the $(N_{B_{IV}})_{Na}$ increase shown in Figure 10, as x increases.

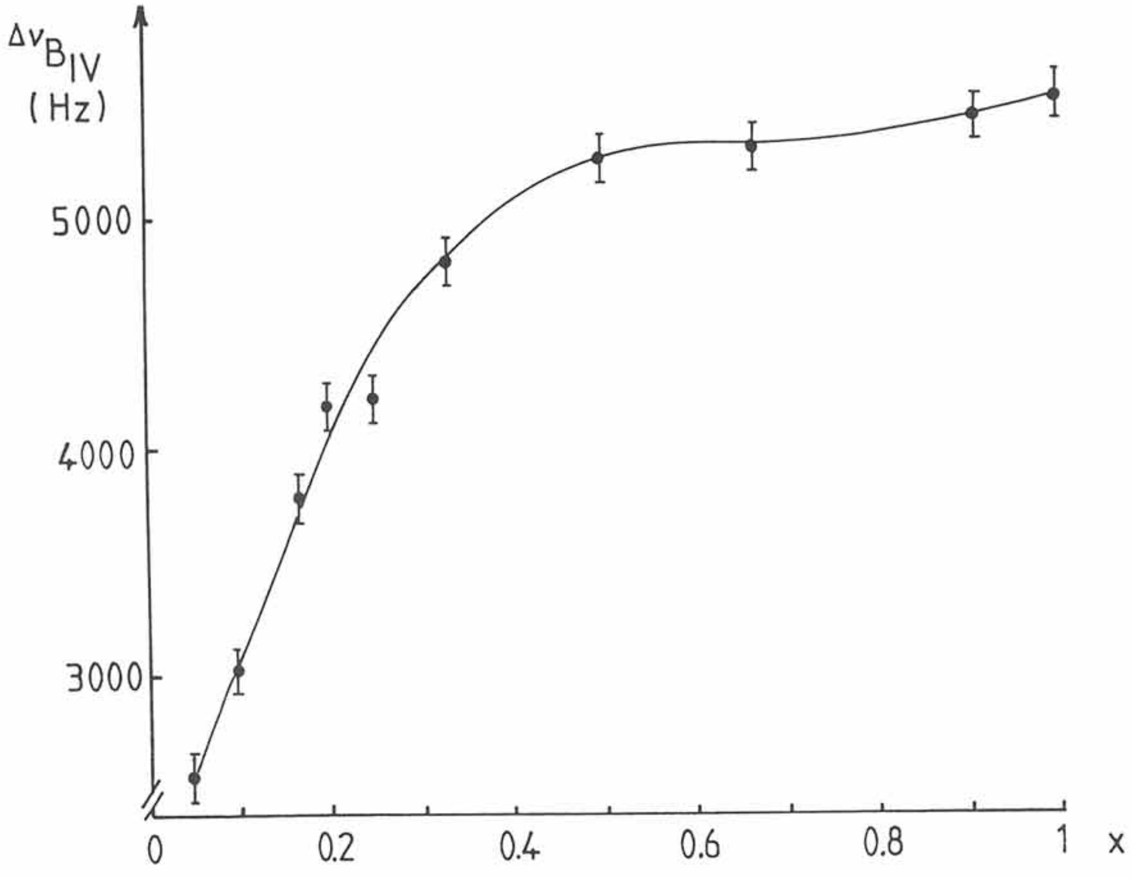

Figure 11-Evolution of width at half-height of the $^{11}B_{IV}$ resonance line ($\Delta\nu_{B_{IV}}$) as a function of x.

4-STRUCTURAL DISCUSSION

From ^{31}P MAS and ^{11}B NMR data, we can suggest structural hypotheses about the arrangement of the various identified units as a function of the composition of the borophosphate glasses.

At the first addition of $Na_2B_4O_7$, all the boron atoms have the four-fold coordination. Each $B_{IV}O_{4/2}^-$ unit could be compensated by one $P_cO_{4/2}^+$ unit as in crystalline BPO_4 [22]. However, we note no ^{31}P MAS NMR line for these glasses in chemical shift region corresponding to BPO_4. We can deduce that the phosphorus atoms are not surrounded by four bridging oxygen atoms in the phosphate units playing the compensator role. So, two species of MB_1 units could exist with probably an overlapping of two signals. The first one, with the $BOPO_2^-OP$ formula, has been suggested in Table 3. The other one, forming the Cp units, and having no equivalent in the former-rich borophosphate glasses [2], would have the $B_cOP_cO_2^{2-}OP$ unit formula (MB_1'). $O_{3/2}B_cOP_cO^{2-}O_{1/2}$ would correspond to the Cp unit. Owing to these data, four ends of the phosphate chains probably formed during the glass preparation (melting and cooling) are interconnected by one boron atom in four-fold coordination inducing a three-dimensional ramification.

In the intermediate compositional range (0.05<x<0.20), the polyphosphate chains have disappeared. All the quasi total $BO_{4/2}^-$ units are always compensated by $(O_{2/2}PO_2^{2-}, 2Na^+)^+$, as mentioned already, forming not only MB_1 and MB_1' but also, MB_2 ($BOPO_2^-OB$) and MB_2' ($B_cOP_cO_2^{2-}OB$) progressively, as x increases. The consequence is a random ramification of the glass network which is liable for an anomalous behaviour of physical and chemical properties such as: undetectable recrystallization temperature, strengthening of microhardness and very weak solubility in water [1].

For x>0.20, the only ^{31}P MAS NMR signal assigned to MB_2 and/or MB_2' units seems to indicate that the phosphorus atoms, in smaller and smaller content, are isolated into borate network containing more and more B_{III} and $(B_{IV})_{Na}$ atoms. Although no NMR information have been supplied to us about the arrangement of borate units, it is reasonable to think that the boron atoms in three and four-fold coordinations form cyclic borate entities as in vitreous $Na_2B_4O_7$. For the borate-rich glass compositions, the phosphorus atoms would mainly be connected around the various borate groups (EB units). A little part would either play the bridge role between these borate groups (MB_2 and /or MB_2') or be located out of the borate network in monomer form (MO units).

5-CONCLUSIONS

^{31}P MAS and ^{11}B NMR have been used for structural investigations on the glass samples with the following chemical composition: $(1-x)NaPO_3+xNa_2B_4O_7$.

This technique has given us information about the close environment of these two glass former atoms. Moreover, it has allowed to determine the fraction of $BO_{4/2}^-$ units compensated by Na^+ ions or by phosphate units. The interpretation of these NMR results made it possible to suggest some structural hypotheses for these glasses, as a function of the composition x.

Starting from the pure metaphosphate vitreous $NaPO_3$ (x=0) made of finite $(O_2PO_{2/2})_n^{n-}$ chains (n≈20), the addition of $Na_2B_4O_7$ up to x = 0.20 (i.e. corresponding to the ratio B/B+P = 0.50) progressively produces a shortening of the chain lengths, leading to "single" $O_2PO_{2/2}^-$ and $O_2P_cO_{2/2}^{2-}$-units for x≤0.20. The borate groups, mainly under the $B_cO_{4/2}^-$ form compensated by $(O_{2/2}PO_2^{2-}, 2Na^+)^+$ units, are used as branching units between chains, with probably a tendency of random ramification with phosphate groups, resulting in the formation of borophosphate groups of the form: $B_cOP_cO_2^{2-}OP$ (MB_1') and $BOPO_2^-OP$ (MB_1) then $B_cOP_cO_2^{2-}OB$ (MB_2') and $BOPO_2^-OB$ (MB_2), as x increases.

In the borate rich concentration range (0.20<x≤1), borate groups including B_{IV} and B_{III} atoms such as those found in pure vitreous $Na_2B_4O_7$, would be considered. The phosphate units, which of course progressively disappear as x increases, bridge the borate groups. However, for the lower phosphate concentrations (i.e. x≥ 0.90), $O_3PO_{1/2}^{2-}$ end groups and / or PO_4^{3-} isolated monomers may be present in the glass.

These structural hypotheses are now confirmed by infrared absorption and Raman scattering techniques which will be presented elsewhere for the sake of the longer range order [23].

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B-2-ETUDE PAR ABSORPTION INFRAROUGE ET DIFFUSION RAMAN

A partir des résultats de RMN (^{31}P MAS et ^{11}B), nous renseignant sur l'environnement immédiat des atomes de bore et de phosphore dans les verres de composition (1-x) $NaPO_3$ x $Na_2B_4O_7$, des hypothèses structurales ont pu être proposées, en fonction de x.

Deux grandes régions structurales ont pu ainsi être distinguées:

i) $x<0.20$

Lorsque x augmente, les unités phosphatées PO_4 appartiennent à des chaînons phosphatés de plus en plus courts en s'entourant d'un nombre croissant d'atomes de bore principalement tétracoordinés. La charge négative de l'unité BO_4 est compensée par celle positive de l'unité PO_4 (formation d'entité de type Cp).

ii) $x>0.20$

Les atomes de bore sont sous la forme d'unités BO_3 et BO_4 en quantité quasi équivalente formant probablement des entités cycliques boratées entre lesquelles semblent s'insérer des unités PO_4, "isolées". La charge négative de l'unité BO_4 est principalement compensée par la présence d'un ion sodium à proximité. Pour les valeurs de x élevées, on note la présence de quelques monomères phosphatés.

Afin d'obtenir des informations plus détaillées sur l'arrangement des différentes unités boratées et phosphatées identifiées dans ces verres par RMN , une étude par spectroscopies d'absorption IR et diffusion RAMAN a été entreprise.

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STRUCTURAL STUDY OF BOROPHOSPHATE GLASSES BY RAMAN AND INFRARED SPECTROSCOPY.

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Abstract.

A structural study by infrared and Raman spectroscopy of the series of glasses with compositions $(1-x)$ $NaPO_3$ - x $Na_2B_4O_7$ *has been carried out. In addition to the usual vibrational modes occuring for* $R \geq 1$ *in the* R Na_2O-P_2O_5 *system (i.e.* νPO_2, νPOP, νPO_3 *and* νPO_4 *of middle, end and monomeric units), typical modes corresponding to borophosphate groups (boron-bonded middle phosphate units) have been identified. In conjonction with previous NMR results, a structural approach can be proposed as a function of the composition x. The addition of* $Na_2B_4O_7$ *up to* $x=0.2$ *induces a shortening of the metaphosphate chains length. The borate groups, mainly under the* $B_{IV}O_{4/2}^-$ *form, are used as branching units between chains, with the formation of borophosphate groups such as:* $(O_{3/2}B_{IV}OPO_{5/2})^{2-}$ *and* $(O_{3/2}B_{IV}OPO_{4/2})^-$ *. Another group, in minor quantity,* $(O_{2/2}B_{III}OPO_{5/2})^-$ *also appears for higher x values. In the borate rich concentration range* $(0.20 \leq x \leq 1)$*, six - membered borate rings including* B_{IV} *and* B_{III} *atoms such as those found in pure vitreous* $Na_2B_4O_7$*, are present. The phosphate units, which of course progressively disappear as x increases, bridge the borate groups. For the lower phosphate concentrations (i.e.* $x \approx 0.90$*),* $O_3PO_{1/2}^{2-}$ *end units connected to the borate groups and* PO_4^{3-} *isolated monomers may be present in the glass.*

1-INTRODUCTION.

In a recent paper [1], the effect of addition of sodium tetraborate ($Na_2B_4O_7$) to sodium metaphosphate ($NaPO_3$) glasses has been studied and an "anomalous" behaviour in properties such as glass transition and crystallization temperatures, density , molar volume , microhardness , water resistance and ultra violet edge absorption has been observed.

It is well known that the addition of an alkali oxide modifier (M_2O) to B_2O_3 glass promotes the conversion of boron atoms from three-fold (B_{III}) to four-fold (B_{IV}) coordination [2]. On the other hand, the addition of M_2O modifier to P_2O_5 results in a "depolymerization" of the three-dimensional glassy network [3]. If R designates the M_2O / P_2O_5 molar ratio, the glasses with $R<1$ correspond to ultraphosphates; those with $R = 1$ have the metaphosphate composition and these latter are built-up from quasi-infinite $(PO_3)_n^{n-}$ chains. For higher values of R, shorter phosphate entities appear, such as $P_4O_{13}^{6-}$ ($R = 1.5$), $P_3O_{10}^{5-}$ ($R = 1.66$)..., carrying increasing negative charges per phosphate unit as the phosphate chains are shortened.

Most of the structural information found in the literature on borophophate glasses concerns glass former (B_2O_3-P_2O_5) rich compositions. In particular, ^{11}B NMR studies suggest that BO_4 units, different from those found in the pure borates, exist in the borophosphates [4,5]. Also, some features of the Raman spectra collected in lithium and silver borophosphates have been interpreted in terms of existence of "P-O-B" groups where the excess of the negative charge of $B_{IV}O_{4/2}^-$ unit is compensated by the excess of the positive charge of $PO_{4/2}^+$ (called B_c and P_c subsequently in the text) [6-8].

Structural information is practically missing for the modifier-rich borophosphate glasses, i.e. corresponding to compositions between $NaPO_3$ and $Na_2B_4O_7$ close to the Na_2O - B_2O_3 - P_2O_5 glass domain limit. Thus, this paper is devoted to an investigation of a series of glasses with compositions (1-x) $NaPO_3$ - x $Na_2B_4O_7$, by means of infrared absorption and Raman scattering experiments; as a matter of fact, these techniques are widely used for structural studies of glasses [9].

2-EXPERIMENTAL DETAILS.

Glasses with composition (1-x) $NaPO_3$ - x $Na_2B_4O_7$ have been prepared as described previously [1]; their composition ($0 \leq x \leq 1$) are listed in Table 1.

N°	x (Mol. fraction)	B/B+P
1	0.00	0.000
2	0.02	0.075
3	0.05	0.173
4	0.10	0.308
5	0.13	0.374
6	0.17	0.450
7	0.25	0.571
8	0.33	0.667
9	0.50	0.800
10	0.67	0.889
11	0.90	0.973
12	1.00	1.000

Table 1-Glass compositions (1-x) $NaPO_3$ - x $Na_2B_4O_7$ of the studied samples by Raman and Infrared spectroscopy.

The infrared spectra have been recorded in the frequency range from 200 to 1600 cm^{-1} on a double beam Perkin - Elmer model 983 grating spectrometer, by using glass powders dispersed in nujol, in cells.

The Raman spectra have been recorded on a Dilor Z 24 triple - monochromator instrument, coupled with an argon ion laser Spectra - Physics model 171; a cooled Hamamatsu photomultiplier coupled with a photon - counting system was used for detection. The colourless glass samples have been cut in shape of parallelepipeds of dimensions about 10 x 10 x 10 mm^3 and with surface carefully polished. Right angle scattering geometries have been adopted with parallel (VV) and perpendicular (VH) polarizations of incident and scattered beams. The 514.5 nm argon emission line has been used for excitation, with incident powers ranging from 100 to 300 mW; the spectral resolution was of about 2.5 cm^{-1}.

3-RESULTS AND DISCUSSION.

In Figure 1, we have represented the infrared absorption spectra of the glass samples corresponding to the different compositions given in Table 1, together with a schematic representation of the infrared spectra of crystalline $Na_4P_2O_7$ and $Na_5P_3O_{10}$ [10]. The positions and assignments of the absorption bands of vitreous $NaPO_3$ [11] and $Na_2B_4O_7$ [12, 13] are summarized in Table 2.

Frequency (cm^{-1})	**Band vibration assignment**	**Frequency (cm^{-1})**
$NaPO_3$ [11]		**$Na_2B_4O_7$ [12, 13]**
	νBO^- (BO_3 in various borate rings)	1450-1300
~1300	$\nu_{as}PO_2$ or $\nu P{=}O$ [15]	
1170-1100	$\nu_s PO_2$	
	νBO_4 (di-, tri-, tetra-, pentaborate groups)	1050-850
1000-870	$\nu_{as}POP$	
800-700	$\nu_s POP$	
	δBOB (O_2B-O-BO_3)	760
	δBOB (O_2B-O-BO_2)	730-700
600-450	δPO_2 and δPOP	

Table 2-Position and assignment of IR absorption bands of vitreous $NaPO_3$ and $Na_2B_4O_7$.

The parallel (VV) and perpendicular (VH) polarized Raman spectra of these glasses are shown in Figures 2. The observed Raman lines have been labelled (a), (b),...; they are represented schematically in Figure 3, together with the Raman line positions of crystalline $Na_4P_2O_7$, $Na_5P_3O_{10}$ [10] and of a glass sample with composition $Na_6P_4O_{13}$ [11]. The assignments of Raman lines of vitreous $NaPO_3$ [11] and $Na_2B_4O_7$ [12, 13] are summarized in Table 3.

From a general point of view, and as usually observed with inorganic glasses, the infrared absorption spectra exhibit broad and overlapping bands, whereas rather narrow lines are observed on the Raman spectra of the same glass samples, thus allowing much precise

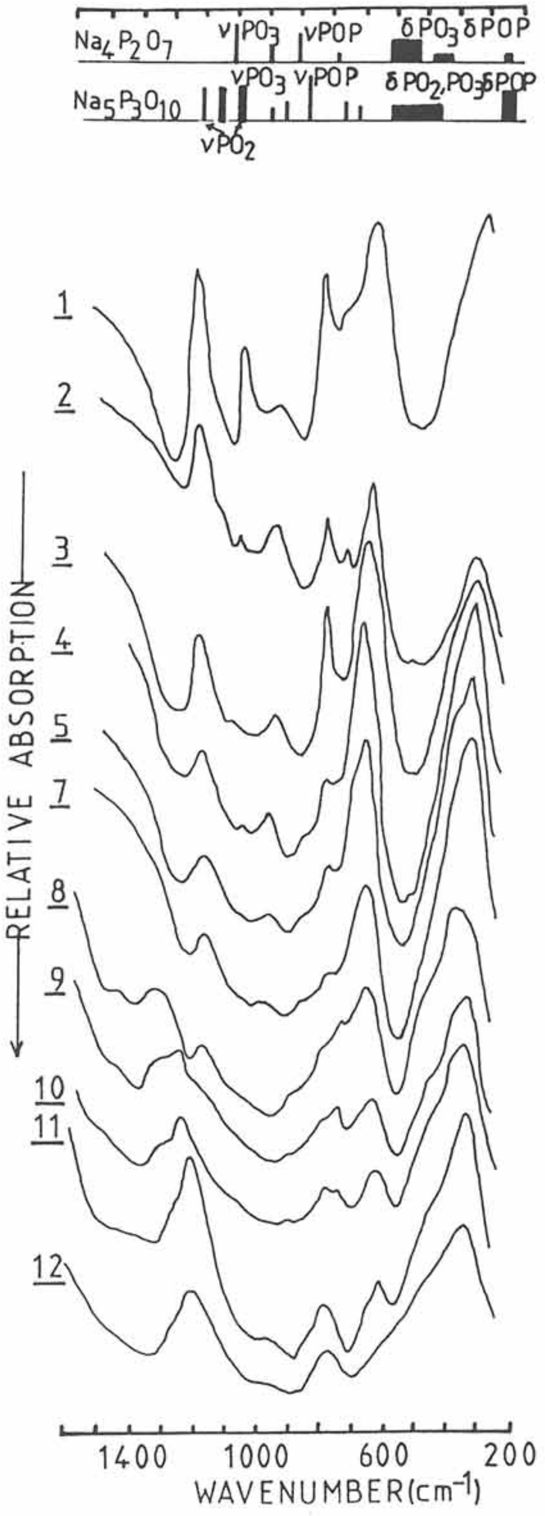


Figure 1-Infrared absorption spectra of (1-x) $NaPO_3$ - x $Na_2B_4O_7$ compositional glass samples (see Table 1); comparison with schematic absorption bands of $Na_4P_2O_7$ and $Na_5P_3O_{10}$ crystalline phases [11].

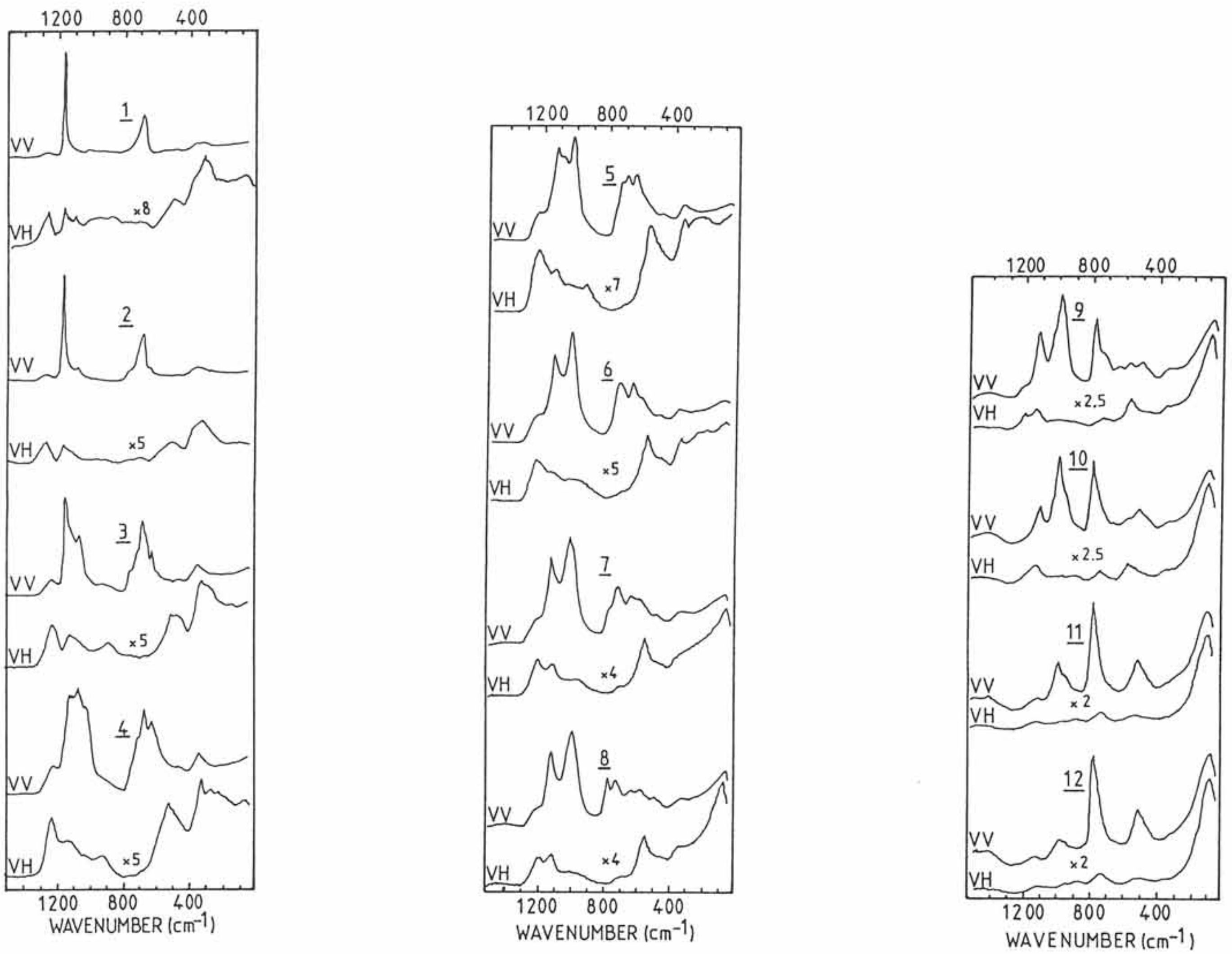


Figure 2-Raman spectra (VV and VH) of (1-x) $NaPO_3$ - x $Na_2B_4O_7$ compositional glass samples (see Table 1).

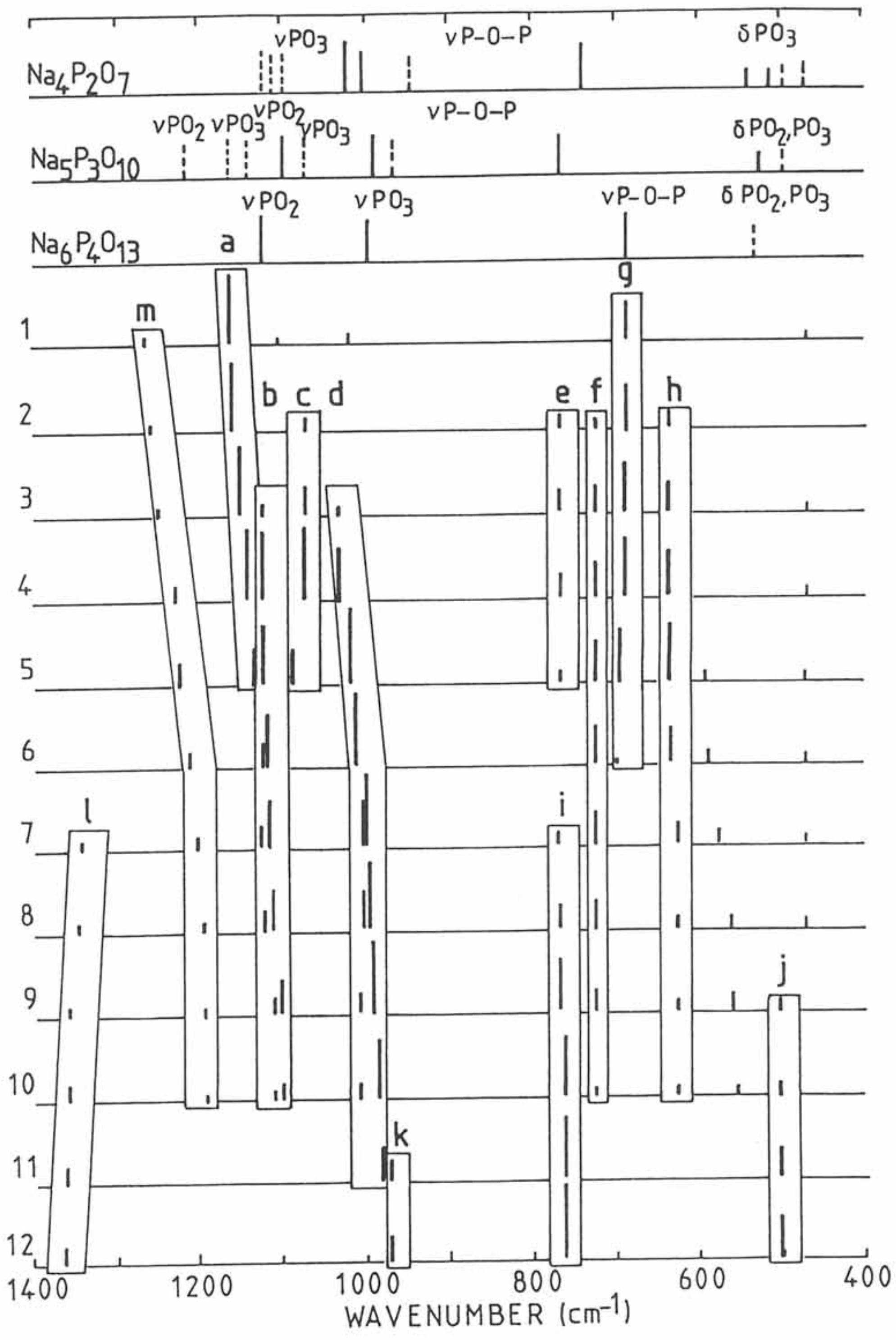


Figure 3-Schematic observed Raman spectra (VV) (Figure 2) of (1-x) $NaPO_3$ - x $Na_2B_4O_7$ compositional glass samples (see Table 1); comparison with crystalline $Na_4P_2O_7$, $Na_5P_3O_{10}$ [10] and with a glass sample of composition $Na_6P_4O_{13}$ [11]. Full line: ν_s and dashed line: ν_{as} of VV spectra.

assignments. Moreover, the Raman spectra are strongly polarized, which means that most of characteristic features are generally present on the VV spectra. Marked spectral evolutions are noticed in both infrared and Raman spectra, as a function of glass composition. It is worth noting that the glass composition $x = 0.20$ corresponds to equal concentrations of boron and phosphorus atoms ($B/B+P = 0.5$); thus, it is not very surprising that the general features observed for the glasses with $0 \leq x \leq 0.20$ are more "phosphate - like", whereas those observed for the glasses with $0.20 \leq x \leq 1.0$ are more "borate - like".

Frequency (cm^{-1})	**Band vibration assignment**	**Frequency (cm^{-1})**
$NaPO_3$ [11]		**$Na_2B_4O_7$ [12, 13]**
	νBO^- (BO_3 in various borate rings)	~ 1400
1270	$\nu_{as}PO_2$	
1170	ν_sPO_2	
	Diborate groups	1120
	ν"breathing"of di-, tri-,pentaborate groups	770
685	ν_sPOP	
	"isolated "diborate groups	500

Table 3-Position and assignment of main Raman lines of vitreous $NaPO_3$ and $Na_2B_4O_7$.

3-1-Glasses with $0 \leq x \leq 0.20$ (samples 1to 6).

Let us first examine the Raman spectrum of the pure phosphate glass $NaPO_3$ (sample 1). This spectrum (VV) is dominated by two strong lines situated at 1164 (line (a)) and 685 cm^{-1} (line (g)) (Figures 2 and 3), assigned respectively to the symmetric stretching modes ν_s (PO_2) and ν_s (POP) of quasi infinite metaphosphate chains $(O_2PO_{2/2})_n{}^{n-}$ [11]; a weak line at 1269 cm^{-1} and a broad band at ~ 940 cm^{-1} correspond to the antisymmetric stretching modes ν_{as} (PO_2) and ν_{as} (POP), respectively. Moreover, there is an additional weak line at 1016 cm^{-1} (Figures 2 and 3) that we assign to the symmetric stretching mode ν_s (PO_3) of $O_3PO_{1/2}{}^{2-}$ end units in agreement with ^{31}P NMR experiments where a small amount of such end groups has been seen in vitreous $NaPO_3$ [14]. This means that the phosphate chains have finite lengths (n ≈ 20 in average [14]); as a consequence, for charge compensation, a few "neutral" $O{=}PO_{3/2}$ (as much as $O_3PO_{1/2}{}^{2-}$ ends) branching different chains may be present and, if such was the case, the characteristic ν (P=O) frequency of these groups could be superimposed on the weak ν_{as} (PO_2) line at 1269 cm^{-1}, as found in ultraphosphates [15]. However, according to NMR data [14], there is no hint of evidence of $O{=}PO_{3/2}$ groups branching phosphate chains; thus, charge compensation is more likely achieved by the presence in the phosphate chains of a few OH groups which, generally, cannot be easily eliminated completely or P_2O_5 losses during the melting. The assignment of the infrared bands observed with vitreous $NaPO_3$ (Figure 1), consistent with a structure made of quasi - infinite chains, is given in Table 2 [11,16].

At the first addition of $Na_2B_4O_7$ (Figures 2 and 3, samples 2 and 3), we notice the disappearence of ν_s (PO_3) at 1016 cm^{-1} and the appearence of new lines (b), (c) and (d) in the ν_s (PO_2) frequency range and (e), (f) and (h) in the ν_s (POP) frequency range. As the $Na_2B_4O_7$ concentration increases up to x=0.20 we observe intensity and frequency variations of these lines, and also a progressive shift and intensity increase of the line at ~ 1270-1210 cm^{-1} (Figure 2 and 3, samples 2 to 6). In the concentration range $0 \leq x \leq 0.20$, there is no hint of existence of ν (B–O) modes in the 1400-1500 cm^{-1} region, characteristic of non - bridging oxygen atoms of borate units [12, 13]. Thus, we conclude that all boron atoms bear bridging oxygen atoms only. On the other hand, from ^{11}B NMR experiments, we know that for very small values of x, practically all boron atoms have the four - fold coordination [14].

So, in sample 2, the borate groups are essentially of the form $B_{IV}O_{4/2}{}^-$ and necessarily, they are used as branching points between phosphate chains, i.e. anywhere in these chains and, on occasion, at the chain ends (disappearence of ν_s (PO_3)). Charge compensation implies again the existence of "neutral" $O{=}PO_{3/2}$ groups, in the proportion of one per two $B_{IV}O_{4/2}{}^-$ following the schematic relation:

(10)

$$(1\text{-}x)\ NaPO_3 + x\ Na_2B_4O_7 \rightarrow (1 - 3x)\ O_2PO_{2/2}{}^- + \mathbf{2x}\ O{=}PO_{3/2} + \mathbf{4x}\ B_{IV}O_{4/2}{}^- + (1+x)\ Na^+ \quad (1)$$

0,8 0,2 0,4 0,4 0,8

4 1 2 2 (1

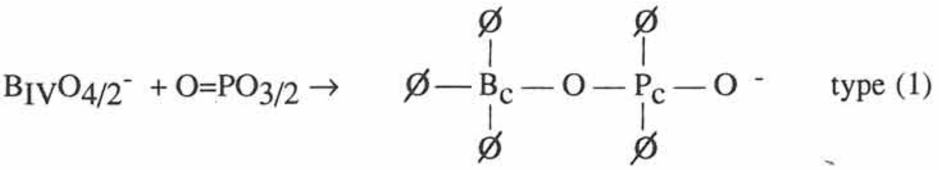
0,6 3

This process should be continued with increasing values of x, but it is some what attenuated by the presence of three - fold coordinated boron atoms ($B_{III}O_{3/2}$ "neutral" groups) whose proportion $B_{III}/B_{III}+B_{IV}$ progressively increases to ≈ 25% as x increases up to 0.20, as shown by NMR experiments [14]. Thus at the particular composition x = 0.20 (B/B+P=0.5), the glass structure can be formally schematized as:

1 3
2 2

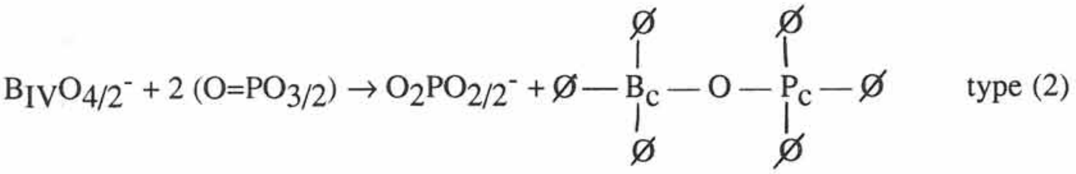
$$Na_2B_4O_7 + 4\,NaPO_3 \rightarrow 6\,Na^+ + B_{III}O_{3/2} + 3\,B_{IV}O_{4/2}^- + O{=}PO_{3/2} + 3\,O_2PO_{2/2}^- \quad (2)$$

However, as mentioned previously, there is no hint of existence of $O{=}PO_{3/2}$ "branching" groups on NMR spectra in the whole glass concentration range [14]; thus, one has to admit that $O{=}PO_{3/2}$ units are directly connected with $B_{IV}O_{4/2}^-$ units, so as to form "boro - phosphate" groups, possibly according to the scheme:



$$B_{IV}O_{4/2}^- + O{=}PO_{3/2} \rightarrow \varnothing - \underset{\varnothing}{\overset{\varnothing}{B_c}} - O - \underset{\varnothing}{\overset{\varnothing}{P_c}} - O^- \qquad \text{type (1)}$$

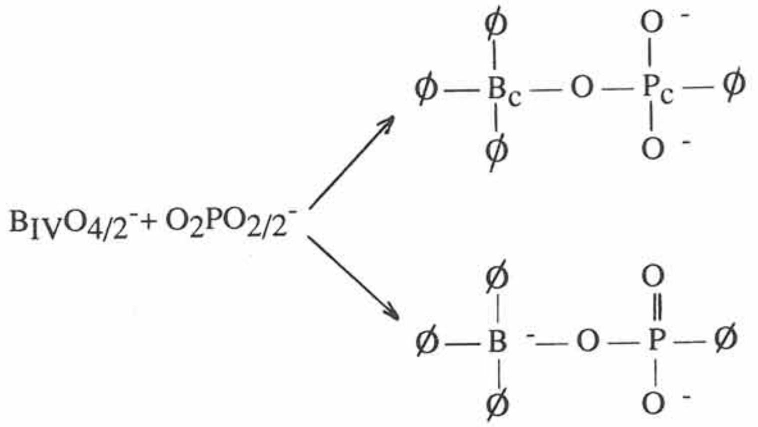
An other possibility can also be considered:



$$B_{IV}O_{4/2}^- + 2\,(O{=}PO_{3/2}) \rightarrow O_2PO_{2/2}^- + \varnothing - \underset{\varnothing}{\overset{\varnothing}{B_c}} - O - \underset{\varnothing}{\overset{\varnothing}{P_c}} - \varnothing \qquad \text{type (2)}$$

In the type (2) , $P_cO_{4/2}^+$ unit is compensator of $B_{IV}O_{4/2}^-$ unit such as in crystalline BPO_4 [17]. Note however that this species seems to be ruled out according to NMR results [14].

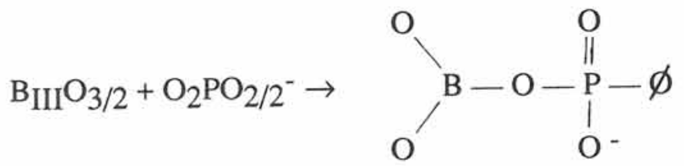
In the same time, the metaphosphate units $O_2PO_{2/2}^-$ may also be associated with borate units in order to form "borophosphate" groups according to the scheme:



type (3a)

type (3b)

or, for higher values of x:



type (4)

Hence, the increasing intensity of the Raman line at ~ 1270 - 1210 cm^{-1} (line (m)) as x increases may be assigned to the presence of the ν (P-O$^-$) vibrations of borophosphate groups, type 1, superimposed on the ν_{as} (PO$_2$) modes of metaphosphate units.

According to these schemes, the different lines (a), (b), (c) and (d) (Figures 2 and 3) are assigned to ν_s (PO$_2$) frequencies of metaphosphate $O_2PO_{2/2}^-$ units in different geometric situations. Obviously, line (a) which is present in pure NaPO$_3$, is assigned to ν_s (PO$_2$) of metaphosphate chains, as mentioned already. The shift of this line to lower frequency, together with the decrease of its intensity as x increases, are due to a shortening of the chains; as a matter of fact, line (a) disappears around x ≈ 0.17. Indeed, the bonding oxygen atoms surrounding boron atoms are always superior to those surrounding phosphorus atoms and this induces the disappearence of the P - O - P bonds before x = 0.2, where B and P atoms are in equal proportion. The line (g), that follows the same intensity variation, is due to the ν_s (POP) stretch of phosphate chains.

The lines (b), (c) and (d) have no equivalent in phosphate glasses with R>1 [17], so that they are assigned to various phosphate units connected to borate units or borophosphate groups. Line (c), appearing at the first addition of Na$_2$B$_4$O$_7$ and disappearing before x = 0.20

is probably due to ν_s (PO_2) of a phosphate unit in borophosphate groups, type (3a), connected with another phosphate group; the corresponding P-O-P symmetric stretch is assigned to line (e), which follows the same intensity evolution as a function of x (Figure 3). The lines (b) and (d), emerging for higher x values (samples 3), which persist for concentrations $x>0.20$ (see section 3-2) may be assigned to the $\nu_s(PO_2)$ modes of phosphate units in borophosphate groups, types (3a) and (3b), connected with $B_{IV}O_{4/2}^-$ unit. The corresponding B-O-P stretching modes are assigned to lines (f) and (h).

As mentioned already, the infrared spectra of these glasses (Figure 1) reveal broad features which cannot be precisely assigned; however, general trends consistent with the interpretation of the Raman spectra are noticed:

i)- absence of ν(B-O) modes with non - bridging oxygen atoms (expected at ≈ 1400 - 1500 cm^{-1}) in the whole concentration range ($0 \leq x \leq 0.20$).

ii)- appearance of new (partially resolved) bands in the $\nu_{as}(PO_2)$ (≈ 1300 cm^{-1}), $\nu_s(PO_2)$ (≈ 1150 cm^{-1}), ν_{as}(P-O-P) (≈ 900 cm^{-1}) and ν_s(P-O-P) (≈ 700 cm^{-1}) frequency ranges, consistent with the presence of new phosphate or borophosphate units, just as described previously.

3-2 Glasses with $0.20 \leq x \leq 1$ (samples 7 to 12).

The major changes observed on the Raman spectra of "borate - like" glasses, i.e. with composition $0.20 \leq x \leq 1$ (Figures 2 and 3) are the appearance of new lines (i), (j) and (l), which persist on the spectrum of the pure borate $Na_2B_4O_7$ ($x = 1$). At the same time, the lines (b), (d), (f) and (h) progressively disappear as x increases up to $x = 1$.

The line (i) is assigned [12, 13] to the "breathing" vibrations of six - membered borate cycles containing both three and four coordinated B_{III} and B_{IV} atoms, and the line (l) to B-O stretching mode involving non - bridging oxygen atoms. As a matter of fact, we known from NMR data that the ratio $B_{III}/B_{III} + B_{IV}$ still increases to ≈ 0.50 as x increases up to 1 [14]. As mentioned already in section 3-1, the lines (b) and (d) are due to ν_s (PO_2) vibrations of phosphate units sandwiched between two borate groups of various kinds, which is quite reasonable in the borate rich concentration range. Note however that these two lines seem to be split in samples 7 to 10 (Figure 2).This splitting would be associated to the presence of $B_{III}O_{3/2}$ units which are connected to the phosphate units in the borophosphate groups, types (3a) and (3b), and / or to the ν_s (PO_2) vibrations in type (4) groups. However, the persistence of the line (d) in sample 11, situated in a range frequency rather low for a $\nu_s(PO_2)$ mode would be assigned to the $\nu_s(PO_3)$ of $O_3PO_{1/2}{}^{2-}$ end units connected to a borate ring and / or to the symmetric stretch of isolated $PO_4{}^{3-}$ "monomers" [6] in accordance with the NMR results [14]. The couple of lines at ~ 500 cm^{-1} (line (j)), is not clearly assigned, however it may be associated with isolated diborate groups [12, 13]. Finally, the assignment of line (k) at ~ 970 cm^{-1}, characteristic of the pure borate, is not well established [12, 13].

Again, the interpretation of the infrared spectra (Figure 1) is not obvious due to the overlapping of broad bands (see Table 2).

4-CONCLUSIONS.

The vibrational (infrared and Raman) study of glasses belonging to the (1 - x) $NaPO_3$ - x $Na_2B_4O_7$ system, in conjunction with NMR results obtained previously [14], made it possible to propose a structural approach for glasses, as a function of the composition x.

Starting from the pure metaphosphate glassy $NaPO_3$ (x = 0) made of quasi - infinite $(O_2PO_{2/2})_n{}^{n-}$ chains, the addition of $Na_2B_4O_7$ up to x = 0.20 (i.e. corresponding to the ratio B/B+P = 0.50) produces a shortening of the chain lengths, leading to "single" $O_2PO_{2/2}{}^-$ units for x<0.20. The borate groups, mainly under the $B_{IV}O_{4/2}{}^-$ form, are used as branching units between chains, with probably a tendency of ramification with phosphate groups, resulting in the formation of borophosphate groups of the form: $(O_{3/2}B_{IV}OPO_{5/2})^{2-}$ and $(O_{3/2}B_{IV}OPO_{4/2})^-$. Another group, in minor quantity, $(O_{2/2}B_{III}OPO_{5/2})^-$ also appears for higher x values.

In the borate rich concentration range (0.20 ≤ x ≤ 1), six - membered borate rings including B_{IV} and B_{III} atoms such as found in pure vitreous $Na_2B_4O_7$, are present, together with B-O bonds with non - bridging oxygen atoms. The phosphate units, which of course progressively disappear as x increases, bridge the borate groups. However, for the lower phosphate concentrations (i.e. $x \approx 0.90$), $O_3PO_{1/2}^{2-}$ end groups and / or PO_4^{3-} isolated monomers may be present in the glass.

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C - MODELISATION STRUCTURALE

Les résultats structuraux obtenus successivement par RMN (^{31}P MAS et ^{11}B) et par spectroscopies vibrationnelles (diffusion RAMAN et absorption IR) nous ont renseignés respectivement sur l'environnement immédiat des atomes de bore et de phosphore et l'agencement des polyèdres formés à plus grande distance.

Le comportement anormal des propriétés physico-chimiques de ces verres de composition (1-x) $NaPO_3$-x $Na_2B_4O_7$ a pu être corrélé à leur évolution structurale en fonction de x.

Rappelons que l'incorporation de $Na_2B_4O_7$ dans $NaPO_3$, provoque un raccourcissement progressif des chaînes métaphosphates jusqu'à l'obtention d'unités phosphatées simples, pour des valeurs de x proches de 0,2 .

Les atomes de bore, principalement sous forme d'unités $BO_{4/2}^-$, connectent les entités phosphatées en formant des groupements $(O_{3/2}B_{IV}OPO_{5/2})^{2-}$ et $(O_{3/2}B_{IV}OPO_{4/2})^-$ provoquant ainsi un accroissement du désordre au sein du réseau vitreux. La formation de ces groupements borophosphatés inusuels résulte de la compensation de charge positive d'une unité PO_4 par celle négative d'une unité BO_4 (entité C_P). Les atomes de bore tricoordinés, minoritaires dans ce domaine de composition, forment des unités $(O_{2/2}B_{III}OPO_{5/2})^-$.

Pour des compositions correspondant à $x > 0,2$, les unités BO_3 et BO_4 s'associent pour former des cycles boratés. Les unités phosphatées peuvent ponter ces cycles et former, pour les compositions les plus riches en borate, des unités terminales $O_3PO_{1/2}^{2-}$ et des monomères PO_4^{3-} .

A partir de la synthèse de ces nombreuses informations structurales et en tenant compte de la composition chimique , il nous a paru intéressant de proposer quelques modèles représentatifs de l'évolution structurale de ces verres en fonction de x.

Soumis à *Physics and Chemistry of Glasses*

STRUCTURAL APPROACH OF (1-x) $NaPO_3$ x $Na_2B_4O_7$ COMPOSITIONAL GLASSES.

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Abstract.

Vibrational (infrared and Raman) and NMR (^{31}P MAS, ^{11}B) results of glasses belonging to the (1-x) $NaPO_3$ x $Na_2B_4O_7$ pseudo binary - system are summarized. Three structural models are proposed as a function of x. In the phosphate rich-compositional region, the addition of the $Na_2B_4O_7$ produces a shortening of the metaphosphate chain lengths. The boron atoms, mainly under the $B_{cIV}O_{4/2}^-$ unit form, compensated by phosphate units, interconnect the end of phosphate chains, with a random ramification tendency and the formation of borophosphate groups of the form: $(O_{3/2}B_{cIV}OP_cO_{5/2})^{2-}$. In the intermediate compositional range, the glasses are built up with $B_{IV}O_{4/2}^-$ and / or $B_{III}O_{3/2}$ units which connect short phosphate entities forming $(O_{3/2}B_{cIV}OP_cO_{4/2})^-$ and $(O_{2/2}B_{III}OPO_{5/2})^-$ borophosphate groups. The borate rich -glasses are formed by some phosphate units inserted in "borate - like" network. For the higher borate concentrations, some $O_3PO_{1/2}^{2-}$ end groups and / or PO_4^{3-} isolated monomers may be present in the glass. The physical and chemical properties are correlated with these different structural models.

1-INTRODUCTION

In two recent papers [1, 2], vibrational (infrared and Raman) and NMR (^{31}P MAS, ^{11}B) studies of glasses belonging to the (1-x) $NaPO_3$ x $Na_2B_4O_7$ pseudo binary - system provided structural informations as a function of the composition x. These investigations intended to explain an "anomalous" behaviour in properties such as glass transition (Tg) and crystallization (Tc) temperatures, density (ρ), molar volume (V), microhardness (Hv), solubility in water (S) and ultra violet edge absorption (λ_c) previously observed [3].

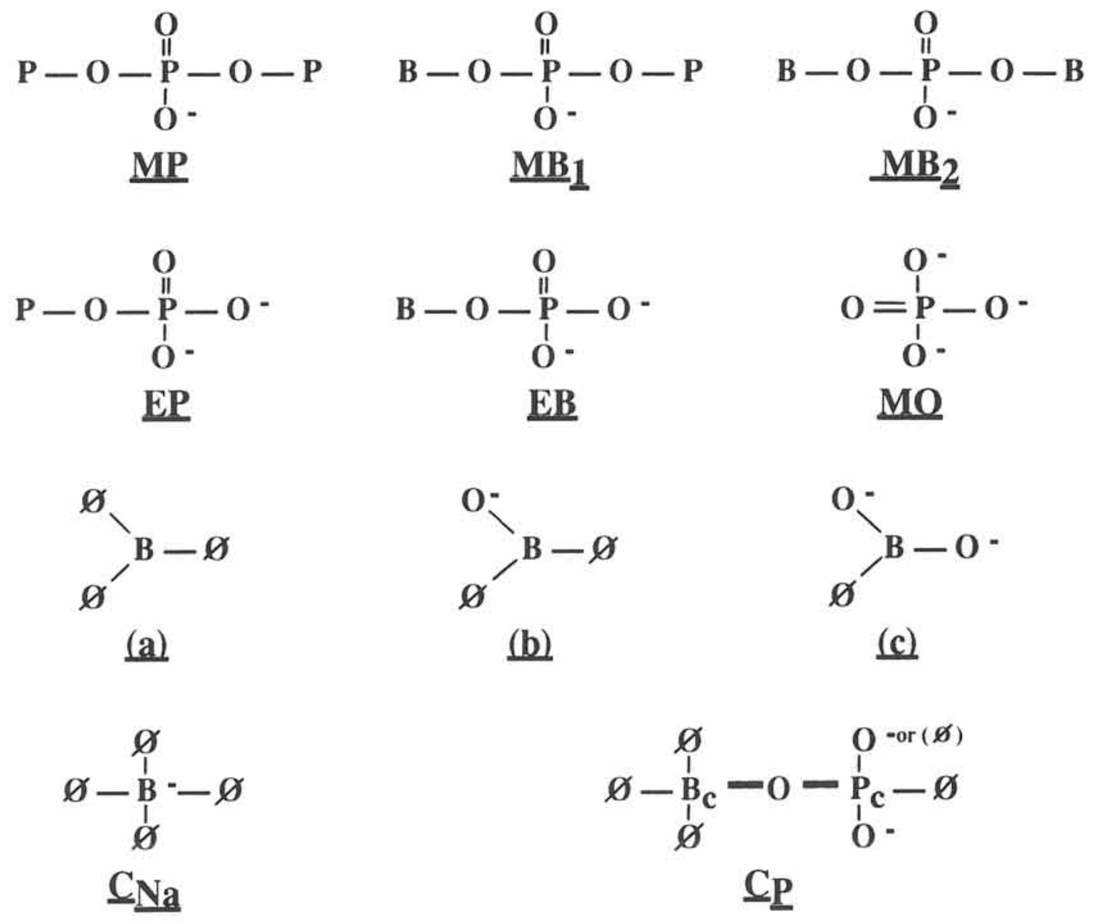


Figure 1-Schematic representation of phosphate, borate and borophosphate units and groups determined by ^{31}P and ^{11}B NMR [2]. The (a), (b) and (c) units cannot be distinguished.

The ^{31}P MAS and ^{11}B NMR results [2] show the existence of several environments of boron and phosphorus atoms (Figure 1). The different phosphate units are:

- the "middle unit" $O_2PO_{2/2}^-$, usually called the metaphosphate unit, connected to, two phosphorus atoms (MP), one phosphorus and one boron atoms (MB_1) or two boron atoms (MB_2) on both sides

- the "end unit" $O_3PO_{1/2}^{2-}$, connected to one phosphorus atom (EP) or one boron atom (EB)

- the "monomer" PO_4^{3-} (MO).

Boron atoms have three and /or four - fold coordinations. The triangular $B_{III}O_{3/2}$ unit can be completely (a) or partially (b, c) surrounded by bridging oxygen atoms. The excess of the negative charge of tetrahedral $B_{IV}O_{4/2}^-$ unit can be compensated either by Na^+ cation (C_{Na}) or by the excess of the positive charge of $(O_{2/2}PO_2^{2-}, 2Na^+)^+$ or $(O_{3/2}PO^-, Na^+)^+$ forming the C_P group. For the last group the boron and the phosphorus atom are called B_c and P_c subsequently in the text.

The interpretation of the Raman and infrared spectra [1] in conjunction with NMR results, (B_{IV}, C_P, MP, EP, MB_1 and / or MB_2, EB and MO proportions), as a function of x, are summarized in Table 1.

From NMR results, we note that:

- the B_{IV} percentage is maximum for the phosphate rich - glasses, decreases and tends to 47.5% for $Na_2B_4O_7$

- the C_P and MP unit percentages rapidly decrease to zero for $x>0.5$ and $x>0.1$ respectively

- the MB_1 and / or MB_2 proportions reach a peak for $x=0.15$, then decrease while the EB units appear and rise 75% for $x=0.9$.

The Raman spectra are dominated by the vibration modes associated with the phosphate units:

-νPO_3 in EP units for $0 \leq x \leq 0.05$ and in EB units for $x>0.9$

-νPO_2 and νPOP of MP units in $(O_2PO_{2/2}^-)_n$ chains for $0 \leq x \leq 0.15$ and then MB_1 units (phosphate chains connected to $B_{IV}O_{4/2}^-$ unit) for $0.02 \leq x \leq 0.15$

-νPO_2 (four modes) in MB_2 units: phosphorus atom connected to two $B_{IV}O_{4/2}^-$ units , for $0.05 \leq x \leq 0.9$ and to one $B_{IV}O_{4/2}^-$ unit and one $B_{III}O_{3/2}$ unit (or two $B_{III}O_{3/2}$ units) , for $0.20 \leq x \leq 0.9$:

	x	0	0.05	0.10	0.15	0.20	0.50	0.90	1.0
NMR	$\%B_{IV}$ ([illegible]	0	100	96	79	70	53	48	47
	$\%C_P$ (C_{iso})	0	100	97	94	86	13		
	%MP	90	31	19					
	%EP	10	1						
	$\%MB_1, MB_2$		68	81	100	95	72	19	
	%EB					5	28	75	
	%MO							6	

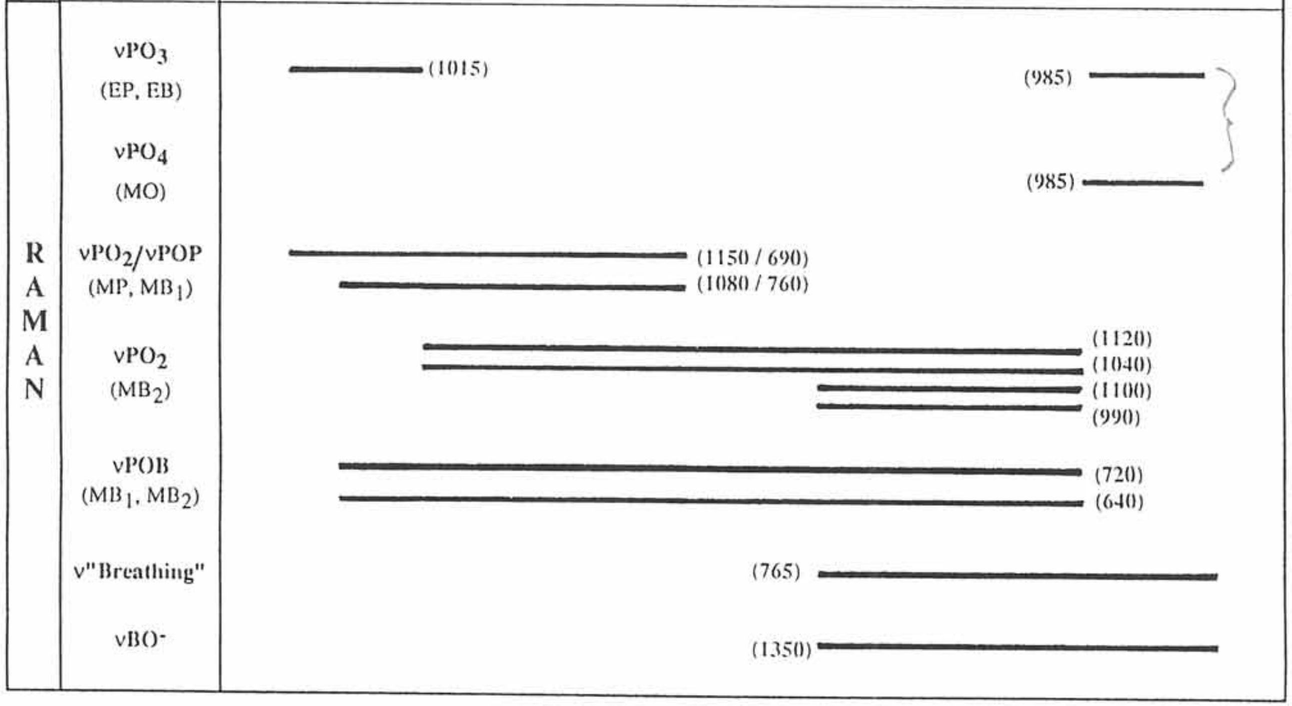


Table 1-Summary of the results obtained by ^{31}P and ^{11}B NMR (proportions of borate, phosphate and borophosphate units and groups) [2] and by Raman spectroscopy (vibrational modes associated with the various borate, phosphate and borophosphate units and groups) as a function of x. The full line and ( ) respectively indicate the compositional range existence and the average position (wavenumber: cm^{-1}) of each vibration mode.

-νPOB (two modes) in MB_1 and MB_2 units for $0.02 < x \leq 0.9$

-νPO_4 in MO units for $0.9 < x < 1.0$

and with the borate units:

-for $0.2 \leq x \leq 1.0$: ν borate cycles "breathing" vibrations and νBO^-.

From these structural informations and in accordance with the chemical composition of each considered glass, we will propose three structural models belonging to the (1-x) $NaPO_3$ x $Na_2B_4O_7$ glass system corresponding to $0 \leq x < 0.05$, $0.05 \leq x \leq 0.2$ and $0.2 < x \leq 1.0$ compositional ranges. Moreover, we will try to correlate the different structural behaviours with the physical and chemical properties.

2-STRUCTURAL MODELS

Three principal structural domains, belonging to the (1-x) $NaPO_3$ x $Na_2B_4O_7$ glass system, can be identified.

2-1- $0 \leq x \leq 0.05$ glass range

The sodium metaphosphate glass is formed by the connection of n ($O_2PO_{2/2}^-$, Na^+) (MP) units forming finite length chains ($n \approx 20$, from NMR results) with some EP units (10%).

The glassy sodium tetraborate is made of the association of dipentaborate, triborate, ditriborate and perhaps diborate cyclic groups (Figure 2), in which the boron atoms are in three and four-fold coordination, approximately in equal proportion [4].

At the first addition of $Na_2B_4O_7$, all the boron atoms are in four - fold coordination and interconnect the phosphate chains. This is revealed by:

i)-the gradual MP units substitution by MB_1 units (^{31}P MAS NMR; Table 1 and Figure 1).

ii)-the new bands on Raman spectra corresponding to νPO_2 (1080 cm^{-1}), νPOP (760 cm^{-1}) and νPOB (720 and 640 cm^{-1}) modes in MB_1 units (Raman: Table 1).

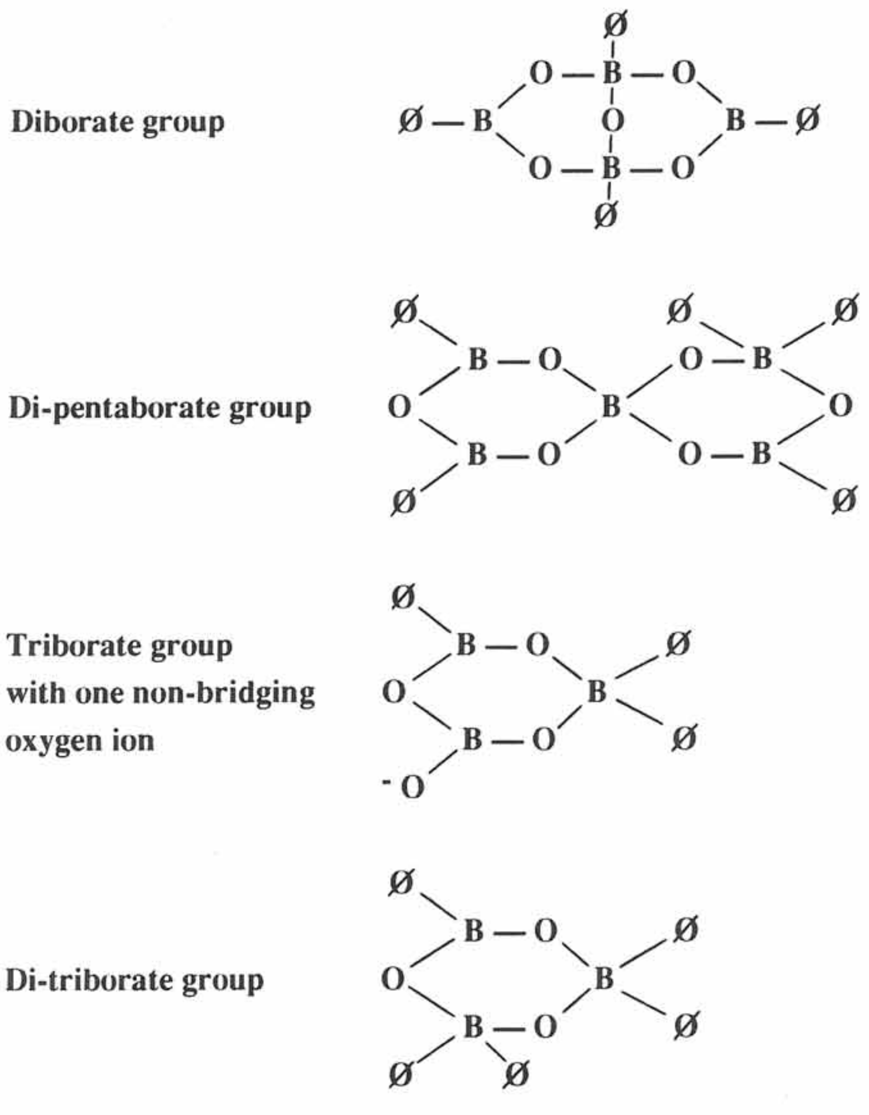


Figure 2-Schematic representation of groups probably present in glassy $Na_2B_4O_7$ and in "borate like" network.

The disappearance of EP units, for x≈0.05 (see Table 1), shows that the B_{IV} atoms not only fit into the chains but also at the end of the phosphate chains with C_P unit formation following the reaction scheme:

$$(B_{III}O_{3/2}) + \underset{(EP)}{(O_3PO_{1/2}{}^{2-}, 2Na^+)} \rightarrow (B_{IV}O_{4/2}{}^{-}, Na^+) + \underset{(MP)}{(O_2PO_{2/2}{}^{-}, Na^+)} \qquad (1)$$

$$\rightarrow \underset{(C_P)}{(O_{3/2}B_{cIV}OP_cO_{5/2})^{2-}, 2Na^+}$$

The Cp unit formation between the phosphate chains agrees with the increase of the νPO_2, νPOB and νPOP bands described above.

The addition of $Na_2B_4O_7$ in $NaPO_3$ induces a tridimensional random ramification of the glass network with a shortening of the average phosphate chain length leading to MB_2 units appearance, beyond x=0.05. This structural model (schematized in Figure 3 for x=0.05) agrees with a strenghtening of the physical and chemical properties (Tg, Tc, ρ, Hv and S^{-1} increase) associated with a disorder increase (Tc undetectable) of the glass network [3].

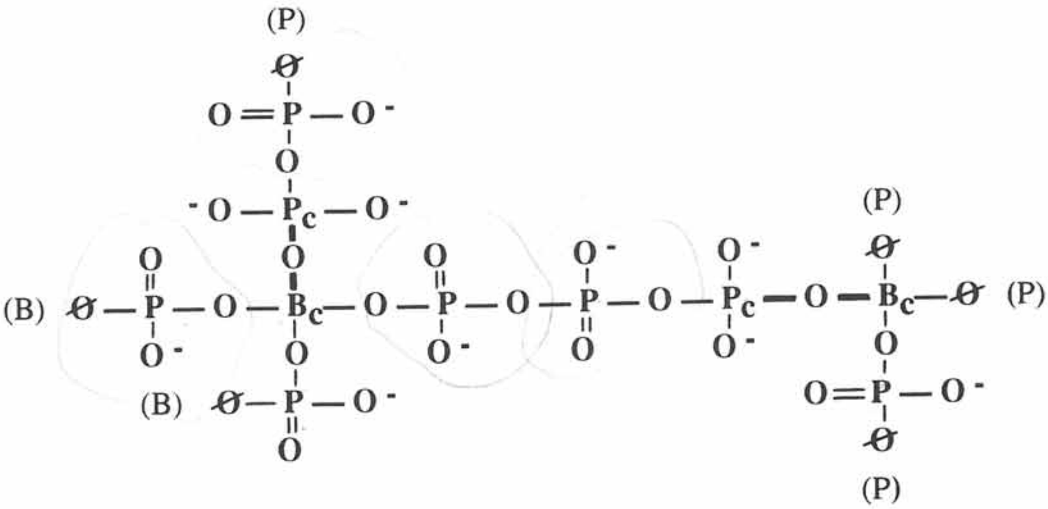


Figure 3-Schematic representation of a "cell" structural model proposed for x=0.05 in the 0 ≤ x ≤ 0.05 glass range. (P) and (B) respectively correspond to the phosphate and borate units belonging to neighbouring "cells".

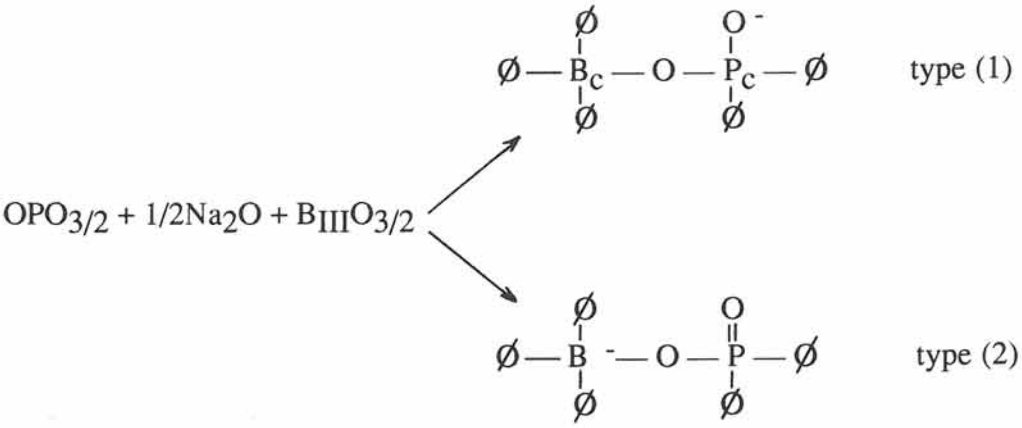
2-2- 0.05 < x ≤ 0.2 glass range

In this compositional range, the phosphate chains length, between the $B_{IV}O_{4/2}{}^{-}$ units, go on decreasing up to obtain only MB_2 units (disappearance of νPO_2 and νPOP vibration modes of MP and MB_1 units from x=0.15, see Table 1). Moreover, the B_{III} atom content rises 25% for x=0.2 and nearly all the B_{IV} atoms are in C_P group form (Figure 1).

As mentioned already, the transformation of B_{III} into B_{IV} atom requires an additional injection of Na^+ cation which cannot happen again according to the equation *(1)* in the absence of EP units. Therefore, it is necessary to consider the PO_4 unit formation with three bridging - oxygen atoms ("branching"units, as in P_2O_5 compound):

$$(O_2PO_{2/2}^-, Na^+) \rightarrow OPO_{3/2} + 1/2Na_2O \qquad (2)$$

which react with $B_{III}O_{3/2}$ unit to form:



Note however that, in the type (2), the "branching" unit $OPO_{3/2}$ seems to be ruled out according to NMR results (see Table 1). Therefore, only type (1) can exist in these glasses. In this type, $[OP_cO_{3/2}^-, Na^+]^+$ may be connected to another $B_{IV}O_{4/2}^-$ unit, forming MB_2 unit, and $B_{cIV}O_{4/2}^-$ may be linked to another phosphate unit. The presence of two νPO_2 vibration modes (1120 and 1040 cm^{-1}) and two νPOB vibration modes (640 and 720 cm^{-1}) is in agreement with the formation of these two complex groups. Indeed, the P_c and P atoms presence involves at once the presence of νP_cO_2, νPO_2, νP_cOB and νPOB vibration modes (Table 1).

On the basis of these informations, it is possible to outline a schematic structural model representative to this glass compositional range and corresponding to x=0.15, as illustrated in Figure 4.

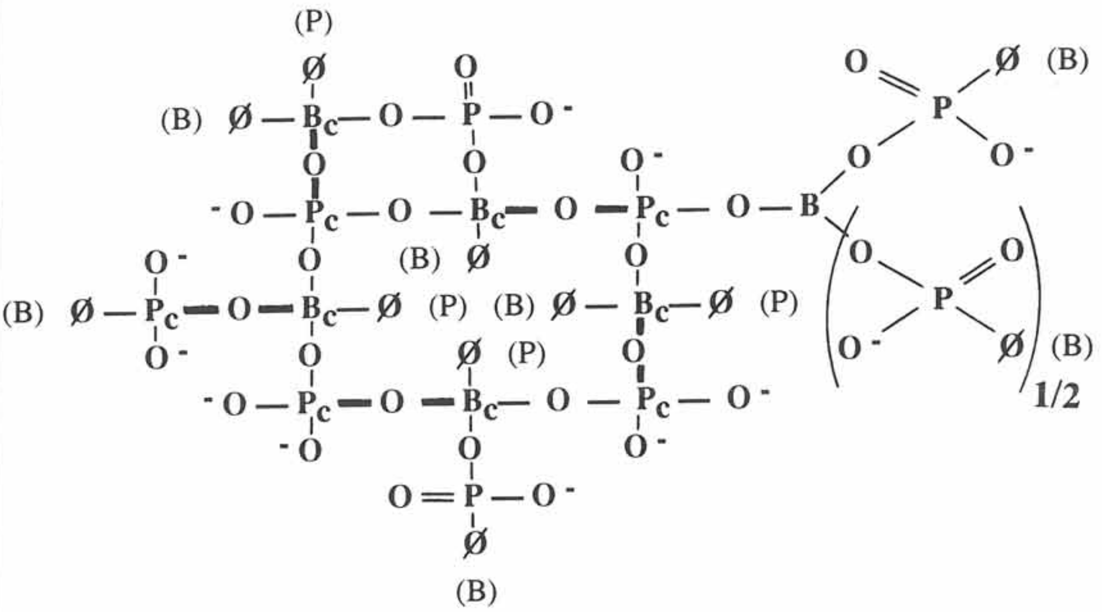


Figure 4-Schematic representation of a "cell" structural model proposed for x=0.15 in the 0.05< x≤ 0.2 glass range. (P) and (B) respectively correspond to the phosphate and borate units belonging to neighbouring "cells"; (*) phosphate unit encountered every other time.

2-3-0.2 < x ≤ 1.0 glass range

For x>0.2 (B/P>1), the increase of the B_{III} atoms in three fold - coordination and the C_{Na} unit number leads to the borate cycle formation (various possible borate groups, see Figure 2) according to Raman results (Table 1). In the same time, a part of phosphate units are more and more isolated between borate cycles leading to the B_{III}-O-P-O-B_{IV}, B_{III}-O-P-O-B_{III} and B_{III}-O-P_c-O-B_{IV} bridge formation in MB_2 unit (new νPO_2 vibration modes at 1100 and 990 cm^{-1}, see Table 1). The other part is in EB form according to the NMR results (Table 1).

Consequently, the borate cycle formation leads to the "borate - like" glass structure. The crossing from a ramified borophosphate to a borate network involves an unhooking of the physical and chemical properties, such as Tg and Hv, for x close to 0.2 [3]. The presence of phosphorus atoms induces, here again, a strong disorder of the structure (T_c undetectable) with a weakening of this glass network (λ_c and S increase) [3]. The borate rich - glass structure, corresponding to x=0.5, is schematized in Figure 5.

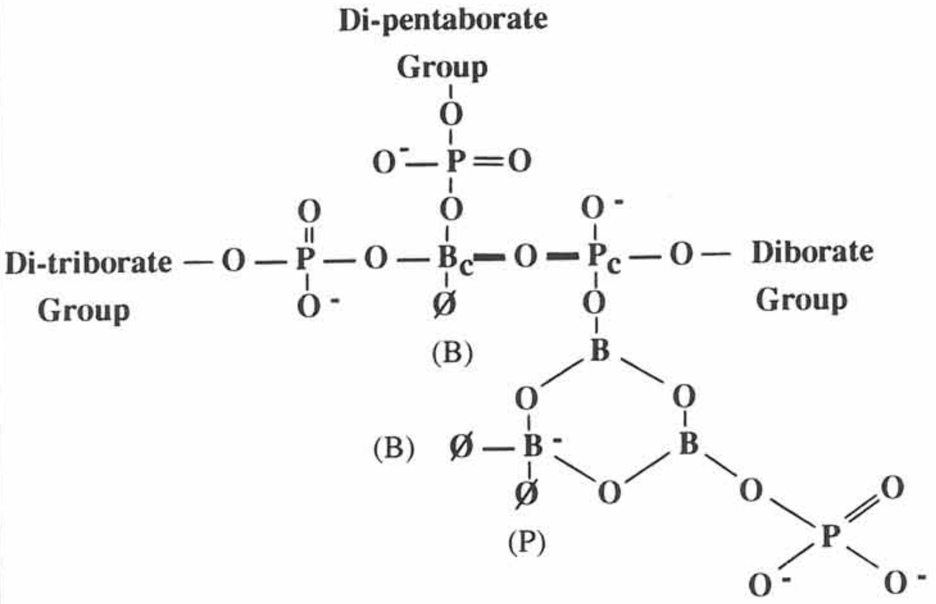


Figure 5-Schematic representation of a "cell" structural model proposed for x=0.5 in the $0.2 < x \le 1.0$ glass range. (P) and (B) respectively correspond to the phosphate and borate units belonging to neighbouring "cells".

According to these structural considerations, described above, a more detailed assignment of Raman vibration modes previously mentioned [1] may be proposed in Table 2.

3-CONCLUSIONS

The study of the compositional (1-x) $NaPO_3$ x $Na_2B_4O_7$ glasses by vibrational infrared and Raman spectroscopy [1] in conjunction with ^{31}P MAS and ^{11}B NMR [2] has

FREQUENCY	ASSIGNMENT
Phosphate vibration modes	
1270 - 1210 cm-1	$\nu P_cO^-$and / or $\nu P{=}O$ and / or $\nu_{as}PO_2$
1165 - 1120 cm^{-1}	$\nu_s PO_2$ in MP chain then MB_1 unit
1120 cm^{-1} / 1100 cm^{-1}	$\nu_s PO_2$ in MB_2 unit with two B_{IV} $\nu_s PO_2$ in MB_2 unit with one B_{IV} and one B_{III} or two B_{III}
1070 - 1085 cm^{-1}	$\nu_s P_cO_2$ in MB_1 unit with one B_{IV}
1040 cm^{-1} / 990 cm^{-1} / 985 cm^{-1}	$\nu_s P_cO_2$ in MB_2 unit with two B_{IV} $\nu_s P_cO_2$ in MB_2 unit with one B_{III} and one B_{IV} $\nu_s PO_3$ in EB and / or $\nu_s PO_4$ in MO unit
1015 cm^{-1}	$\nu_s PO_3$ in EP
Borophosphate vibration modes	
760 cm^{-1}	$\nu_s P_c$-O-P in MB_1 unit
720 - 715 cm^{-1}	$\nu_s P_c$-O-B_c in MB_1 then MB_2 units
685 - 695 cm^{-1}	ν_sP-O-P in MP then MB_1 units
640 - 625 cm^{-1}	ν_sP-O-B in MB_1 then MB_2 units
Borate vibration modes	
1345 - 1385 cm^{-1}	$\nu_s BO^-$
975 cm^{-1}	not well established (existence in pure borate)
765 cm^{-1}	ν"Breathing" of borate cycles (di - penta, ditri, tri and di - borate groups)
500 cm^{-1}	νBOB out side borate cycles (not well established)

Table 2-Attempted assignments and positions of various phosphate, borophosphate and borate vibration modes.

allowed to follow their structural evolution, as a function of x. Three structural models can be proposed:

i) in the $0 \leq x \leq 0.05$ glass range, the addition of $Na_2B_4O_7$ into the glassy $NaPO_3$ made of $(O_2PO_{2/2})_n{}^{n-}$ chains ($n \approx 20$) produces a shortening of the chain lengths. The borate groups, mainly under the $B_{IV}O_{4/2}{}^-$ unit form, are used to branching chain ends with probably a tendency of ramification with phosphate groups, resulting in the formation of borophosphate group of the form: $(O_{3/2}B_{cIV}OP_cO_{5/2})^{2-}$ (C_P group).

ii) in the $0.05 < x \leq 0.2$ glass range, the shortening of the chain lengths and the ramification with phosphate groups are occuring with the formation of new borophosphate group of the form: $(O_{3/2}B_{cIV}OP_cO_{4/2})^-$ (C_P group). Another group, in minor quantity, $(O_{2/2}B_{III}OPO_{5/2})^-$ also appears for x close to 0.2.

iii) in the $0.2 < x \leq 1.0$ glass range, six - membered borate rings, including B_{IV} and B_{III} atoms such as found in pure vitreous $Na_2B_4O_7$, are present, together with B-O bonds with non - bridging oxygen atoms. The phosphate units, which of course progressively disappear as x increases, bridge the borate groups. However, for the higher borate concentrations, some $O_3PO_{1/2}{}^{2-}$ end groups and / or $PO_4{}^{3-}$ isolated monomers may be present in the glass.

The structural evolution proposed above is coherent with the unexpected behaviour of the physical and chemical properties observed in these borophosphate glasses.

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CHAPITRE II

VERRES BOROPHOSPHATES DE SODIUM ET DE CALCIUM

INTRODUCTION DU CHAPITRE II

Le premier chapitre a été consacré à l'étude physico-chimique et structurale des verres de composition (1-x) $NaPO_3$-x $Na_2B_4O_7$, formés par deux composés à fort pouvoir vitrifiant. Elle nous a montré que leur association pouvait donner naissance à des matériaux vitreux possédant des propriétés nettement supérieures à celles des composés $NaPO_3$ et $Na_2B_4O_7$ pris indépendamment; celles-ci découlant d'une structure vitreuse renforcée. Une proposition de modèles structuraux de ces verres a conclu ce travail.

Comme nous l'avions annoncé en introduction de ce mémoire, cette première étude n'était qu'une étape dans la recherche de nouveaux matériaux potentiellement intéressants dans le domaine des biomatériaux. En effet, il nous avait semblé judicieux d'avoir une bonne connaissance de ces verres avant de leur ajouter un troisième composant: l'hydroxyapatite de calcium. Les verres ainsi formés pourraient plus aisément être étudiés et le rôle joué par $Ca_5(PO_4)_3OH$ plus facilement identifié.

L'étude qui suit a donc été, comme pour les verres précédemment étudiés, de déterminer les caractéristiques physico-chimiques d'échantillons issus du domaine vitreux préalablement mis en évidence dans le système $NaPO_3$-$Na_2B_4O_7$-$Ca_5(PO_4)_3OH$.

A - CARACTERISATIONS PHYSICO-CHIMIQUES

Soumis à *Materials Letters*

ADDITIONAL CALCIUM-HYDROXYAPATITE EFFECT ON SODIUM BOROPHOSPHATE GLASSES: Physical and chemical characterizations.

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Abstract.

A narrow vitreous domain along the $NaPO_3$-$Na_2B_4O_7$ *pseudo binary system has been determined in the* $NaPO_3$-$Na_2B_4O_7$-$Ca_5(PO_4)_3OH$ *pseudo ternary system. The addition of* $Ca_5(PO_4)_3OH$ *in the sodium borophosphate glasses induces a strengthening of most of the studied properties such as glass transition temperature, microhardness and water resistance with retention of the unexpected behavior observed in the phosphate rich-domain of the glasses belonging to the* $NaPO_3$-$Na_2B_4O_7$ *system. This strengthening might be due to the "cross linkage " of phosphate and /or borophosphate groups by the* Ca^{2+} *cations.*

1-INTRODUCTION

In a previous paper [1], the effect of equimolar substitution of sodium metaphosphate for sodium borate on the glass transition (Tg) and crystallization (Tc) temperatures, molar volume (V), density (ρ), microhardness (Hv), solubility in water (S) and ultraviolet cut-off wavelength (λc) has been studied. The unexpected behavior observed in these glasses has been correlated with their structural modifications displayed by Raman diffusion and NMR studies [2,3].

Although these glasses have enough good physical and chemical properties for use as biomaterials, it was interesting to improve them by addition of a third compound: calcium hydroxyapatite $Ca_5(PO_4)_3OH$ (called HAp subsequently in the text). Moreover, HAp is the main component of the bone mineral part and its presence should improve the biocompatibility of the obtained glasses.

This paper is devoted to the physical and chemical characterizations of glass samples stemmed from the vitreous domain in the $NaPO_3$-$Na_2B_4O_7$-$Ca_5(PO_4)_3OH$ system. These properties will be compared with those of the sodium borophosphate glasses and the influence of additional HAp will be shown.

2-EXPERIMENTAL

2-1-Preparation

The glass samples studied have been prepared from commercial $NaPO_3$, $Na_2B_4O_7$ and $Ca_5(PO_4)_3OH$ compounds (purity>99.5%). The finely ground mixture, put inside a vitreous carbon crucible, was heated using a HF furnace above the melting temperature (700-1100°C) in argon atmosphere for 10 to 15 mn. All samples were quenched by switching off the heating system. The resulting weigth losses are lower than 1%.

They stem from the vitreous domain of the $NaPO_3$-$Na_2B_4O_7$-$Ca_5(PO_4)_3OH$ pseudo - ternary system (Figure 1) with the composition formula (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$, where R=x/1-x, x corresponding to the fraction of $Na_2B_4O_7$ in the pseudo binary system. Their compositions (X and R values) together with the corresponding B/B+P and Na+Ca/B+P ratio values are reported in Table 1.

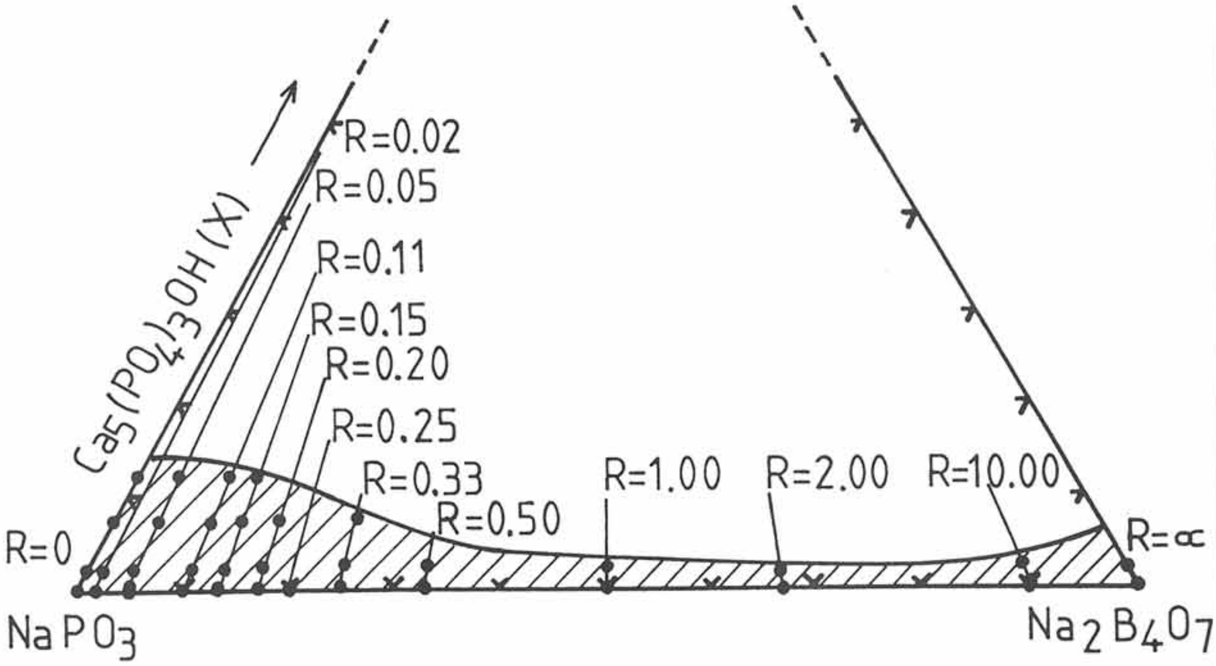

Figure 1-Vitreous domain (hachured domain) and studied glass samples (black point) corresponding to the composition formula (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$.

2-2-Characterizations

2-2-1-Glass transition (T_g) and crystallization (T_c) temperatures

These data have been accurately determined (deviation <5°C) with a DTA Setaram apparatus. The measurements were performed on glass powders introduced in platinum tubes. The heating rate was 350°C. h^{-1} in the 30-900°C range.

X\R	**0**	**0.02**	**0.05**	**0.11**	**0.15**	**0.20**	**0.25**	**0.33**	**0.50**	**1.00**	**2.00**	**10.0**	∝
0	0 1	0.075 0.962	0.167 0.913	0.308 0.846	0.374 0.813	0.444 0.777	0.500 0.750	0.571 0.714	0.667 0.667	0.800 0.600	0.889 0.555	0.968 0.512	1.000 0.500
0.02	0 1.038	0.070 1.001	0.158 0.955	0.294 0.883	0.358 0.849	0.427 0.813		0.552 0.746	0.647 0.696	0.781 0.625	0.871 0.578	0.960 0.531	0.985 0.518
0.07	0 1.123		0.139 1.040	0.262 0.968	0.322 0.932	0.386 0.894		0.506 0.823					
0.12	0 1.194		0.123 1.114	0.234 1.043	0.289 1.007								

Table 1: Composition of the studied glass samples (X and R values), B/B+P and Na+Ca/B+P ratio values corresponding to the (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ formula.

0.167 ← B/B+P
0.913 ← Na+Ca/B+P

2-2-2-Molar volume (V) and density (ρ)

V values are derived from the density measurements (ρ), determined using the hydrostatic pressure concept by immersing the samples in diethyl-orthophthalate. The uncertainty of the measurements is estimated to be ±0.01. g. cm^{-3}.

2-2-3-Microhardness (H_v)

The measurements have been made in the Vickers scale of hardness with a Leitz apparatus. The visualization of the pyramidal stamp has been improved by using a gold coating deposition (~50Å) on the polished surface of the glass sample. The accuracy is ± 10 daN mm^{-2}.

2-2-4-Solubility in water (S)

Samples with parallelepiped shape have been immersed for several days into water (pH=6) at 25°C. The solubility measured in g. cm^{-2}. mn^{-1} was then evaluated by weighing (after careful drying) the undissolved remaining pieces.

3-RESULTS

Figures. 2 - 5 respectively show the evolution of the glass transition (T_g) and crystallization (T_c) temperatures, molar volume (V) and density (ρ), microhardness (H_v) and solubility in water (S) as a function of the B/B+P ratio corresponding to the (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ vitreous compositions.

In a general way, the HAp introduction induces an increase of the above mentioned parameters (Tg, Tc, V, ρ, Hv and S^{-1}) without appreciable change of the anomalous evolution observed in relation with the HAp free-glasses.

Tg (Figure 2) and Hv (Figure 4) have similar evolution. They increase almost linearly with R for B/B+P< 0.5 (R<0.25) and B/B+P>0.6 (R>0.45) and an unhooking occurs between 0.25<R<0.45. The addition of HAp induces an increase of these two parameters, more significant in the phosphate rich-region for which the vitreous domain is more extended.

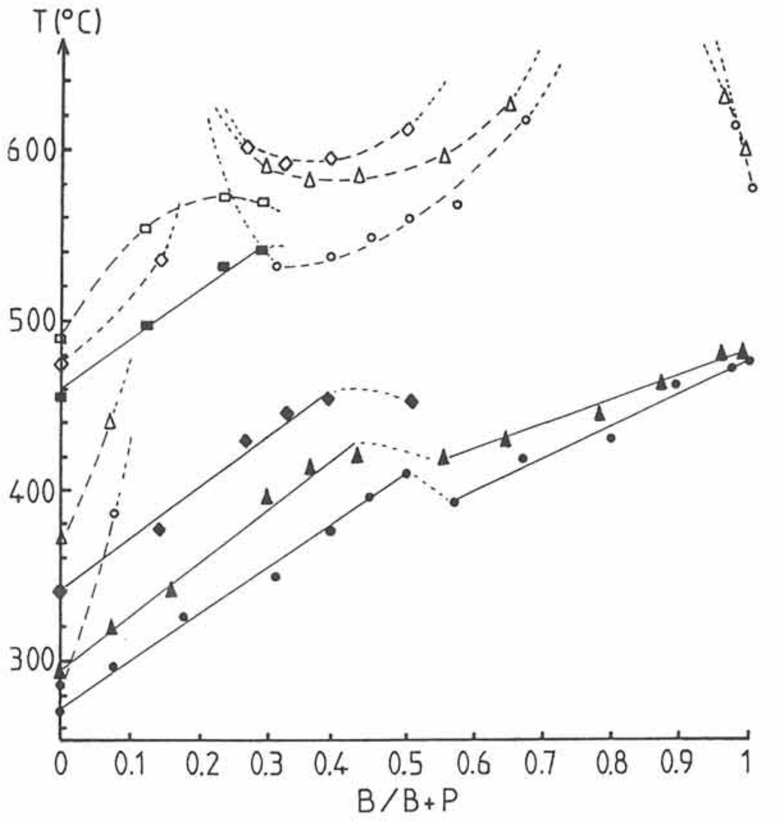

Figure 2-Variation of the glass transition (Tg) and crystallization (Tc) temperatures versus the B/B+P ratio of (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ glass sample composition for X=0 (Tg: •; Tc: o), X=0.02 (▲; Δ), X=0.07 (♦; ◇) and X=0.12 (■; □)

T_c (Figure 2) increases with X and is undetectable up to X=0.07 for the rich- and poor- phosphate compositions. We note that (Tc-Tg) values decrease as X increases.

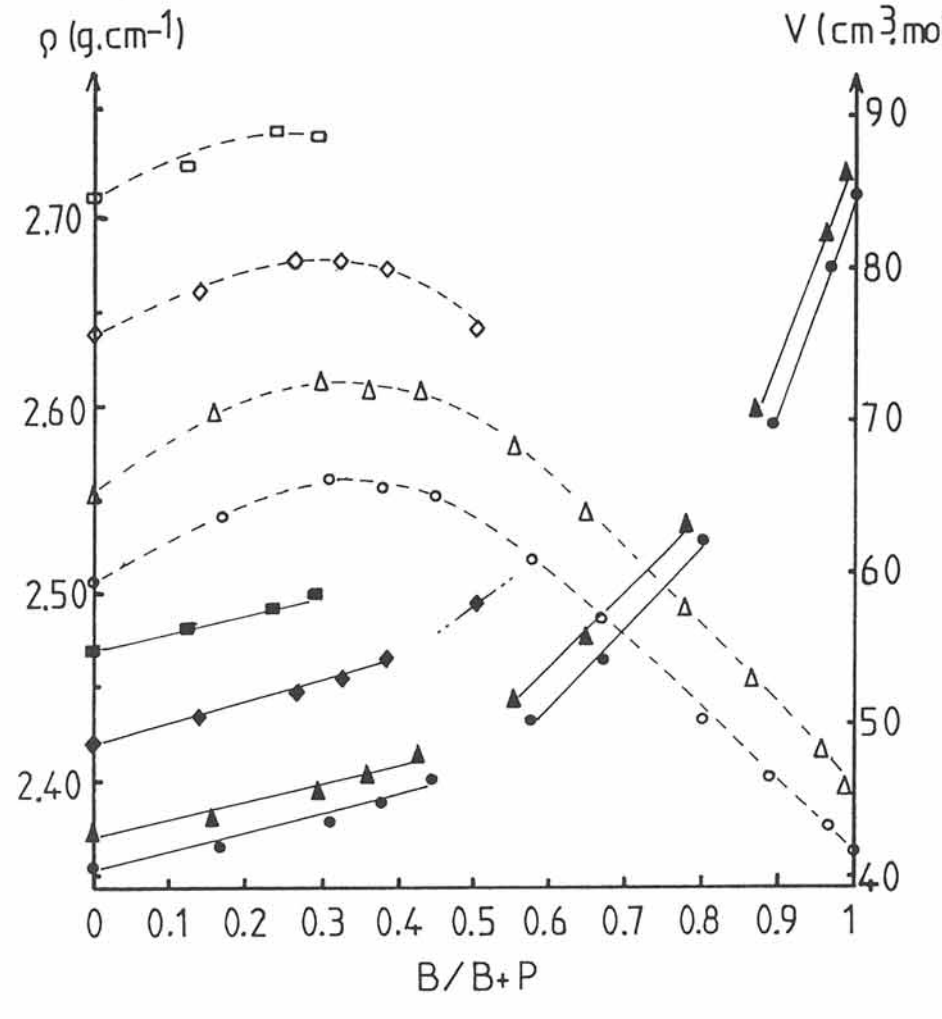

Figure 3-Variation of the molar volume (V) and density (ρ) versus the B/B+P ratio of (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ glass sample composition for X=0 (V: •; ρ: o), X=0.02 (▲; Δ), X=0.07 (◆; ◇) and X=0.12 (■; □)

V (Figure 3) linearly increases with R for B/B+P<0.5, 0.5<B/B+P< 0.8 and B/B+P>0.8 with three distinct slopes in these three glass domains. The adjunct of HAp provokes a regular increase of V (conservation of the slopes in each different glass domain). The ρ value reaches a maximum around B/B+P=0.35 for X=0 which shifts towards the phosphate richer-region as X increases and then rapidly falls down.

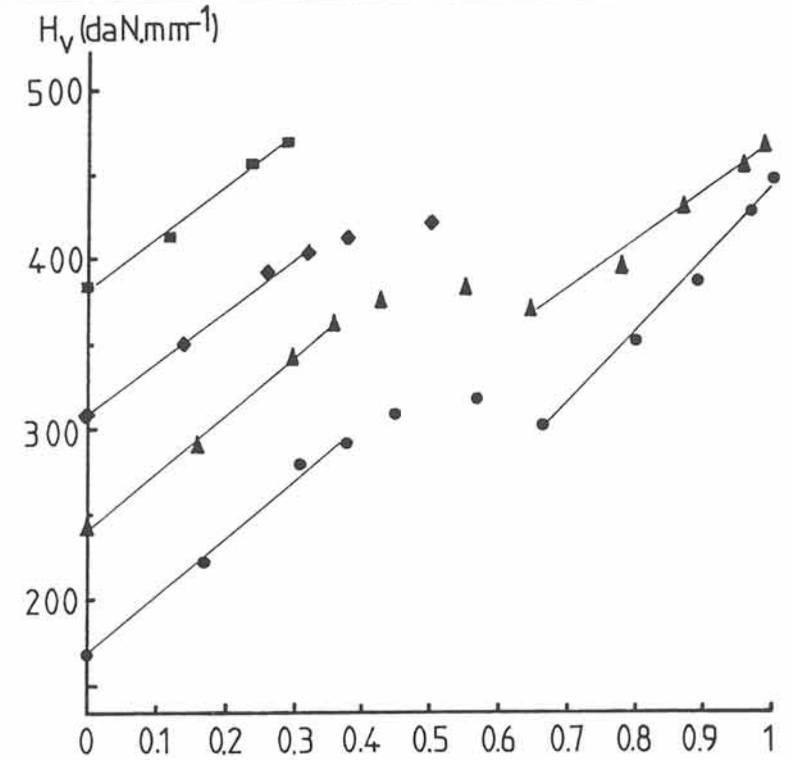

Figure 4-Variation of the microhardness (Hv) versus the B/B+P ratio of (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ glass sample composition for X=0 (●), X=0.02 (▲), X=0.07 (◆) and X=0.12 (▬)

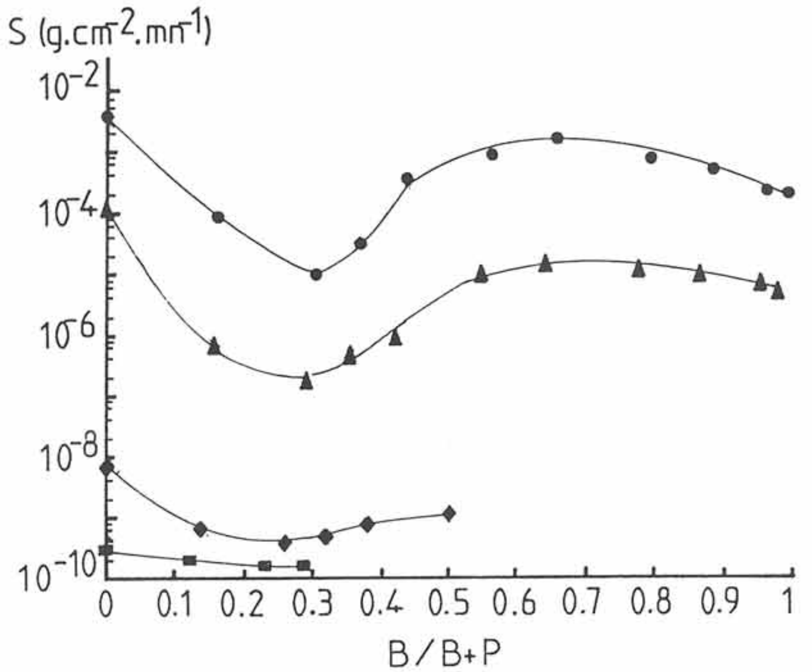

Figure 5-Variation of the solubility in water (S) (T=25°C; pH=6) versus the B/B+P ratio of (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ glass sample composition for X=0 (●), X=0.02 (▲), X=0.07 (◆) and X=0.12 (▬)

S (Figure 5) abruptly decreases for borate poor- compositions and reaches a minimum around B/B+P=0.25 as R and X increase . For the highest borate contents, S mainly exhibits a maximum around B/B+P=0.70 for $X \leq 0.07$.

4-DISCUSSION

It is noteworthy to remark that the deep modifications of the physical and chemical properties depend, in the first place, on the borate content. As mentioned in the previous studies, the unexpected behavior observed in the sodium borophosphate glasses (X=0) has been correlated to structural changes which can be briefly recalled [4].

The addition of $Na_2B_4O_7$ in the pure metaphosphate glassy $NaPO_3$ (R=0) made of quasi-infinite $(O_2PO_{2/2})_n{}^{n-}$ chains produces a shortening of the chain lengths, leading to "single" $O_2PO_{2/2}{}^-$ units for R=0.25. The borate groups mainly under the $BO_{4/2}{}^-$ form are used as branching units between chains inducing a random ramification of the glass network. These structural modifications lead to a Tc undetectable, an increase of compactness, water resistance and microhardness. In the borate rich-glasses, the borate rings including boron atoms in three - and four - fold coordination such as found in pure vitreous $Na_2B_4O_7$, are present. The phosphate units bridge the borate groups and $PO_4{}^{3-}$ monomers appear in the glasses for the phosphate lower compositions. In the intermediate compositional range (around R=0.25), the crossing from a more "borophosphate-like" network to a more "borate-like "network can explain the anomalous behavior such as the unhooking of Tg and Hv evolution.

The HAp addition in the sodium phosphate glasses involves a strong increase of the Na+Ca/P ratio, and therefore a decrease in the glass-former content, probably associated with a shortening of the chains length as usually observed in the MO and M_2O-$P_2 0_5$ systems [5, 6]. Similarly, an identical behavior should occur for the sodocalcic borophosphate glasses. Consequently, we should expect a decrease of physical and chemical properties. So, the decrease of the compactness (V^{-1}) and the glass forming ability (Tc-Tg) probably arise from the "depolymerization" effect due to the HAp addition. But the Ca^{2+} cations might play the role of "cross linkage" of the short borophosphate groups and be at the origin of the strengthening of the microhardness (Hv) and the water resistance (S^{-1}) in the phosphate-rich concentration range. On the contrary, in the borate-rich concentration range, the "cross linkage" effect does not seem to exist and the HAp addition rapidly induces the crystallization leading to the formation of a very narrow vitreous domain.

5-CONCLUSIONS

The physical and chemical characterizations of glass samples having the composition (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ give evidence of a significant increase with X of all the studied properties such as glass transition (Tg) and crystalization (Tc) temperatures, molar volume (V), density (ρ), microhardness (Hv) and water resistance (S^{-1}).

This behavior could be correlated with the following structural expectations:

i) The addition of HAp would induce a significant depolymerization of the borophosphate glass-former network leading to the formation of smaller and smaller borophosphate groups responsible for the decrease of the glass forming ability (Tc-Tg) and the compactness (V^{-1}) and the formation of the narrow vitreous domain along the $NaPO_3$ - $Na_2B_4O_7$ pseudo binary system.

ii) The Ca^{2+} cations could play the role of the "cross linkage" reducing the depolymerization effect, above all in the phosphate-rich concentration range, and responsible for the increase of the microhardness (Hv) and the water resistance (S^{-1}).

These structural considerations are now confirmed by use of NMR and Raman techniques, and will be presented elsewhere for the sake of clarity.

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B - APPROCHE STRUCTURALE

B-1-ETUDE PAR RMN DU ^{31}P (MAS) ET DU ^{11}B

L'étude des propriétés physico-chimiques des verres de composition (1-X) [NaPO$_3$*-R Na*$_2$*B*$_4$*O*$_7$*]-X Ca*$_5$*(PO*$_4$*)*$_3$*OH vient de montrer une augmentation de la température de transition vitreuse et de cristallisation, de la microdureté et de la résistance chimique avec l'addition d'apatite .*

Afin de connaître le rôle joué par l'hydroxyapatite sur le réseau vitreux borophosphaté, nous avons entrepris l'étude structurale de ces verres par RMN (^{31}P *MAS et* ^{11}B*). L'interprétation des résultats, facilitée par l'étude préalable effectuée sur les verres du pseudo-binaire (Chapitre I), nous permettra de corréler structure et propriétés physico-chimiques.*

Soumis à *Journal of Non-Crystalline Solids*

INFLUENCE OF THE ADDITION OF CALCIUM-HYDROXYAPATITE ON SODIUM BOROPHOSPHATE GLASSES.

PART I: ^{31}P AND ^{11}B NMR INVESTIGATIONS.

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Abstract

^{31}P MAS and ^{11}B NMR have been used for structural investigations on the glass samples with chemical composition (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$. The ^{31}P resonance spectra present several Gaussian lines which are due to different types of environment of PO_4 units such as middle (MP), end (EP) and monomeric (MO) units. For the sodocalcicphosphate glasses (R=0), the addition of the hydroxyapatite (HAp) induces a decrease of the MP unit number (i.e. shortening of the length of metaphosphate chains) with an increase of the EP unit number in which the non-bridging oxygen atoms are partially compensated by Ca^{2+} cations which probably "cross-link" the short phosphate chains. From ^{11}B spectra of the sodocalcicborophosphate glasses (R>0), the boron atom fraction in four-fold coordination has been determined. The addition of $Na_2B_4O_7$ also progressively produces a shortening of the length of phosphate chains. As in pure borophosphate glasses (X=0), the borate groups, mainly under the $BO_{4/2}^-$ form compensated by phosphate units, are used as branching units between chains leading to the formation of borophosphate groups of the form: $BOPO_2^{2-}OP$ and $BOPO_2^-OP$ (MB_1) then $BOPO_2^{2-}OB$ and $BOPO_2^-OB$ (MB_2), as R increases up to 0.2. The number of these units decreases as X increases. For the $0.20<R\leq1$ compositional range, borate groups including boron atoms in three- and four-fold coordination such as those found in pure vitreous $Na_2B_4O_7$, would be considered. The phosphate units bridging the borate groups (MB_2) are located out of the borate network and progressively disappear giving place to EB and MO units as R increases. The extent of the vitreous domain and the physical and chemical properties are correlated with these different structures.

1-INTRODUCTION

In a previous paper [1], sodium borophosphate glassy samples, belonging to the (1-x) $NaPO_3$-x $Na_2B_4O_7$ pseudo binary system, have been studied and an "anomalous" behaviour in properties such as glass transition and crystallization temperatures, density , molar volume , microhardness , water resistance and ultra violet edge absorption has been observed. Moreover, NMR (^{31}P MAS, ^{11}B) [2] and vibrational (infrared and Raman) [3] studies have allowed to propose three structural models [4] which have been correlated with the physical and chemical properties, as a function of x.

Although the borophosphate glasses have enough good physical and chemical properties, it was interesting to improve them with the addition of a third compound: Hydroxyapatite $Ca_5(PO_4)_3OH$ (called HAp subsequently in the text), known for its biological role in mineralization of the living hard tissues. So, the obtained new glasses might have biocompatibility properties, as silicophosphate or calciumphosphate multicomponent bioglasses [5].

Recently, a narrow vitreous domain along the $NaPO_3$-$Na_2B_4O_7$ pseudo binary system has been determined in $NaPO_3$-$Na_2B_4O_7$-$Ca_5(PO_4)_3OH$ pseudo ternary system. The physical and chemical characterizations have shown a strengthening of most of the studied properties such as glass transition and crystallization temperatures, microhardness and water resistance [6].

This paper is devoted to the structural investigation of the influence of additional calcium hydroxyapatite in glasses samples using ^{31}P MAS NMR and ^{11}B NMR techniques. The ^{31}P chemical shifts will be related to changes in bonding and environment of the PO_4 units as a function of the glassy composition. The analysis of the profile evolution of ^{11}B NMR lines will lead to the determination of BO_4 unit fraction. The interpretation of NMR data will be based on the previous NMR results obtained for the (1-x) $NaPO_3$-x $Na_2B_4O_7$ compositional glasses [2].

2-EXPERIMENTAL DETAILS

2-1-Preparation

The glass samples studied in this work have been prepared as described previously [1] from commercial $NaPO_3$, $Na_2B_4O_7$ and $Ca_5(PO_4)_3OH$ compounds (purity>99.5%). They stem from the vitreous domain of the $NaPO_3$-$Na_2B_4O_7$-$Ca_5(PO_4)_3OH$ pseudo - ternary system (Figure 1) with the composition (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$, where R=x/1-x, x corresponding to the fraction of $Na_2B_4O_7$ in the pseudo binary system. Their compositions (X and R values) together with the corresponding B/B+P and Na+Ca/B+P ratio values are reported in Table 1.

X\R	**0**	**0.05**	**0.11**	**0.15**	**0.20**	**0.33**	**0.50**	**1.00**	**2.00**	**10.0**	∝
0	0 ***1*** 1	0.167 ***3*** 0.913	0.308 ***4*** 0.846	0.374 ***5*** 0.813	0.444 ***6*** 0.777	0.571 ***7*** 0.714	0.667 ***8*** 0.667	0.800 ***9*** 0.600	0.889 ***10*** 0.555	0.968 ***11*** 0.512	1.000 ***12*** 0.500
0.02	0 ***13*** 1.038	0.158 ***14*** 0.955	0.294 ***15*** 0.883	0.358 ***16*** 0.849	0.427 ***17*** 0.813	0.552 ***18*** 0.746	0.647 ***19*** 0.696	0.781 ***20*** 0.625	0.871 ***21*** 0.578	0.960 ***22*** 0.531	0.985 ***23*** 0.518
0.07	0 ***24*** 1.123	0.139 ***25*** 1.040	0.262 ***26*** 0.968	0.322 ***27*** 0.932	0.386 ***28*** 0.894	0.506 ***29*** 0.823					
0.12	0 ***30*** 1.194	0.123 ***31*** 1.114	0.234 ***32*** 1.043	0.289 ***33*** 1.007							

Table 1: Composition (X and R values), B/B+P and Na+Ca/B+P ratio value corresponding to the glasses samples (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ studied by ^{31}P MAS NMR and ^{11}B NMR.

0.167 ← B/B+P
3 ← Sample number
0.913 ← Na+Ca/B+P

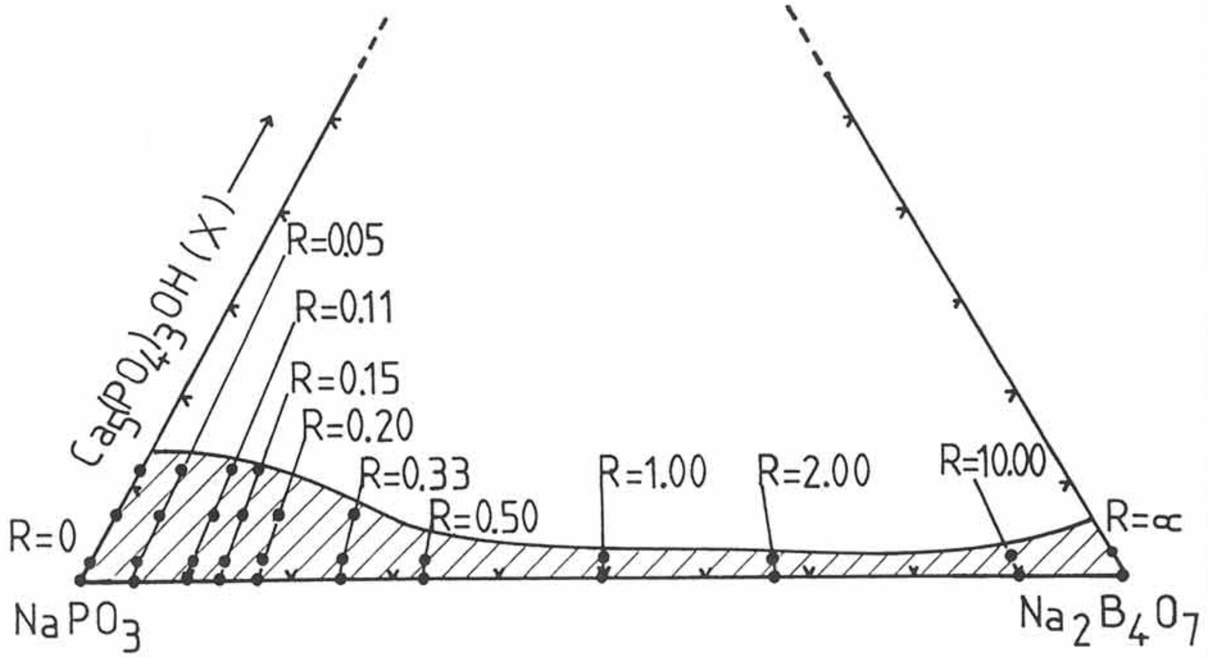


Figure 1-Vitreous domain (hachured domain) and glass samples (black point) corresponding to the composition (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ studied by NMR.

The crystalline $Ca_3(PO_4)_2$ and $Ca_2P_2O_7$ have been prepared, by heating of adequate mixture of $CaCO_3$ and $NH_4H_2PO_4$ commercial compounds (purity >99.5%) at 200°C, 400°C then 900°C under nitrogen flow. The $Ca(PO_3)_2$ glass has been obtained, in a first time, using the above conditions, then melted about 1100°C and finally quenched.

2-2-NMR

^{31}P and ^{11}B NMR spectra were recorded on a high power BRUKER MLS 200 spectrometer equipped with a 4.7 T superconducting magnet.

The single pulse sequence (Px-τ-acquisition) was used for MAS experiments because of long T_1's and compared to cyclops sequence (90°x-τ-acquisition). The chemical shifts of the lines were referenced to 85% phosphoric acid measured in the same probe. The spectrometer operating conditions were as follows:

- -spectrometer frequency: 80.962 MHz
- -pulse program: onepulse and cyclops
  - -pulse-width: 1 µs for onepulse and 3 µs for cyclops
  - -dead time delay: 20 µs
  - -recycle delay time: 60 s
  - -spinning speeds: 4 KHz and 5 KHz
- -spectral width: 125 KHz

The simulation of the ^{31}P NMR lines were performed using the "Linesim" program delivered by BRUKER. This program allows to adjust peak positions, peak heights, line widths, ratios of Gaussian and Lorentzian function and relative proportions of their areas.

^{11}B NMR spectra were recorded using a solid echo sequence ($90°x$-τ-$90°y$-τ'-acquisition) with 8 phase cycling. The spectrometer operating conditions were as follows:

- -spectrometer frequency: 64.168 MHz
- -pulse program:
  - -90° pulse length: 3 µs
  - -recycle time: 60 s
- -spectral width: 500 KHz

3-RESULTS AND DISCUSSION

3-1-^{31}P MAS NMR

The ^{31}P MAS NMR spectra of (1-X) [$NaPO_3$-R $Na_2B_4O_7$]-X $Ca_5(PO_4)_3OH$ compositional glass samples are reported in Figures 2-4, together with the normalized area values of each deconvoluted resonance band schematized by vertical heavy line.

The ^{31}P MAS NMR data for the glass samples corresponding to X=0 ($NaPO_3$-R $Na_2B_4O_7$) have shown the existence of environment changes around phosphorus atoms, as R increases [2]. The structural interpretations are summarized in Table 2. We notice that the MB_1 and MB_2 units can be written in two different forms depending on whether the boron atom in four-fold coordination is compensated by Na^+ (as in Table 2) or by the phosphate unit and become $B_cOP_cO_2^{2-}$-OP (MB_1') and $B_cOP_cO_2^{2-}$-OB (MB_2'). For more detail see ref.[2].

Compositional Range (X=0)	**Symbol**	**Unit type**	**Shift Range (ppm/H_3PO_4)**
0≤R≤0.11	MP	$POPO_2^-$OP	(-20.0, -18.0)
(0≤x≤0.10)	MB_1	$POPO_2^-$OB	(-10.5, -9.5)
	EP	$POPO_3^{2-}$	(2.0, 3.0)
0.11<R<0.33	MB_1	$POPO_2^-$OB	(-9.5, -6.0)
(0.10<x<0.25)	$+MB_2$	$+BOPO_2^-$OB	
0.33≤R<10	MB_2	$BOPO_2^-$OB	(-6.0, -4.0)
(0.25≤x<0.91)	EB	$BOPO_3^{2-}$	(3.5, 5.0)
R≥10	MB_2	$BOPO_2^-$OB	(-4.0)
(x≥0.91)	EB	$BOPO_3^{2-}$	(+5.5)
	MO	PO_4^{3-}	(+16.0)

Table 2: Structural formulas, symbols and chemical shift range of phosphate units as a function of the borophosphate glass composition (X=0). (**P**: considered phosphorus).

For comparison, ^{31}P MAS NMR of glassy $M_{1/m}{}^{m+}(PO_3)^-$ and crystalline $M_{7/m}{}^{m+}(P_5O_{16})^{7-}$, $M_{5/m}{}^{m+}(P_3O_{10})^{5-}$, $M_{4/m}{}^{m+}(P_2O_7)^{4-}$, $M_{3/m}{}^{m+}(PO_4)^{3-}$ [M=Na (m=1) or Ca (m=2)] and HAp have been studied. The assignment of the resonance lines and the corresponding isotropic chemical shifts (δ ppm) are listed in Table 3. We notice that all the calcium phosphate compounds present δ values more negative than those of homologous sodium phosphate compounds.

Compound	Unit type	Isotropic Chemical Shift (ppm/H3PO4)	
		M=Na	M=Ca
$M_{1/m}{}^{m+}(PO_3)^-$ (v)	MP	-20.0 (*)	-27.5 (*)
	EP	+2.0 (*)	-11.3 (*)
$M_{7/m}{}^{m+}(P_5O_{16})^{7-}$ (c)	MP	-16.6 (7)	
	EP	+1.0 (7)	
$M_{5/m}{}^{m+}(P_3O_{10})^{5-}$ (c)	MP	-8.9 (*)	
	EP	-0.2 (*)	
$M_{4/m}{}^{m+}(P_2O_7)^{4-}$ (c)	EP	+1.3 (*)	-8.5 (*)
$M_{3/m}{}^{m+}(PO_4)^{3-}$ (c)	MO	+14.1 (*)	+1.7 (*)
$Ca_5(PO_4)_3OH$ (c)	MO		+3.7 (*)

Table 3:^{31}P NMR isotropic chemical shifts of some homologous crystalline (c) Na- or Ca-polyphosphates and calcium hydroxyapatite and glasses (v). (*) this work.

3-1-1-Sodocalcic phosphate glasses (R=0).

The addition of HAp in sodium metaphosphate (Figure 2) simultaneously induces:

i)- a shift of the two resonance lines towards the more negative δ

ii)- a progressive reversing of these two lines intensity

The decrease of the line close to δ =-20ppm and the increase of the line at δ =+2ppm , assigned respectively to MP and EP units for X=0, show an obvious shortening of the finite metaphosphate chains length $(O_2PO_{2/2})_n{}^{n-}$ (n=20) [2], as X increases. The area ratio of these two resonance lines indicates that the average of the chain length tends to n=3 for X=0.12. The negative shift of the line corresponding to EP units may be due to a progressive partial substitution of Na^+ by Ca^{2+}cations to compensate the charge of non bridging oxygen atoms of the $O_{1/2}PO_3{}^{2-}$ end units in agreement with the result reported in Table 3.

We tentatively explain this result by the formation of two types of new chain ends with the HAp addition. During the melting, the breaks of the long metaphosphate chains may give rise to two different ends of shorter chains which can be formally schematized as:

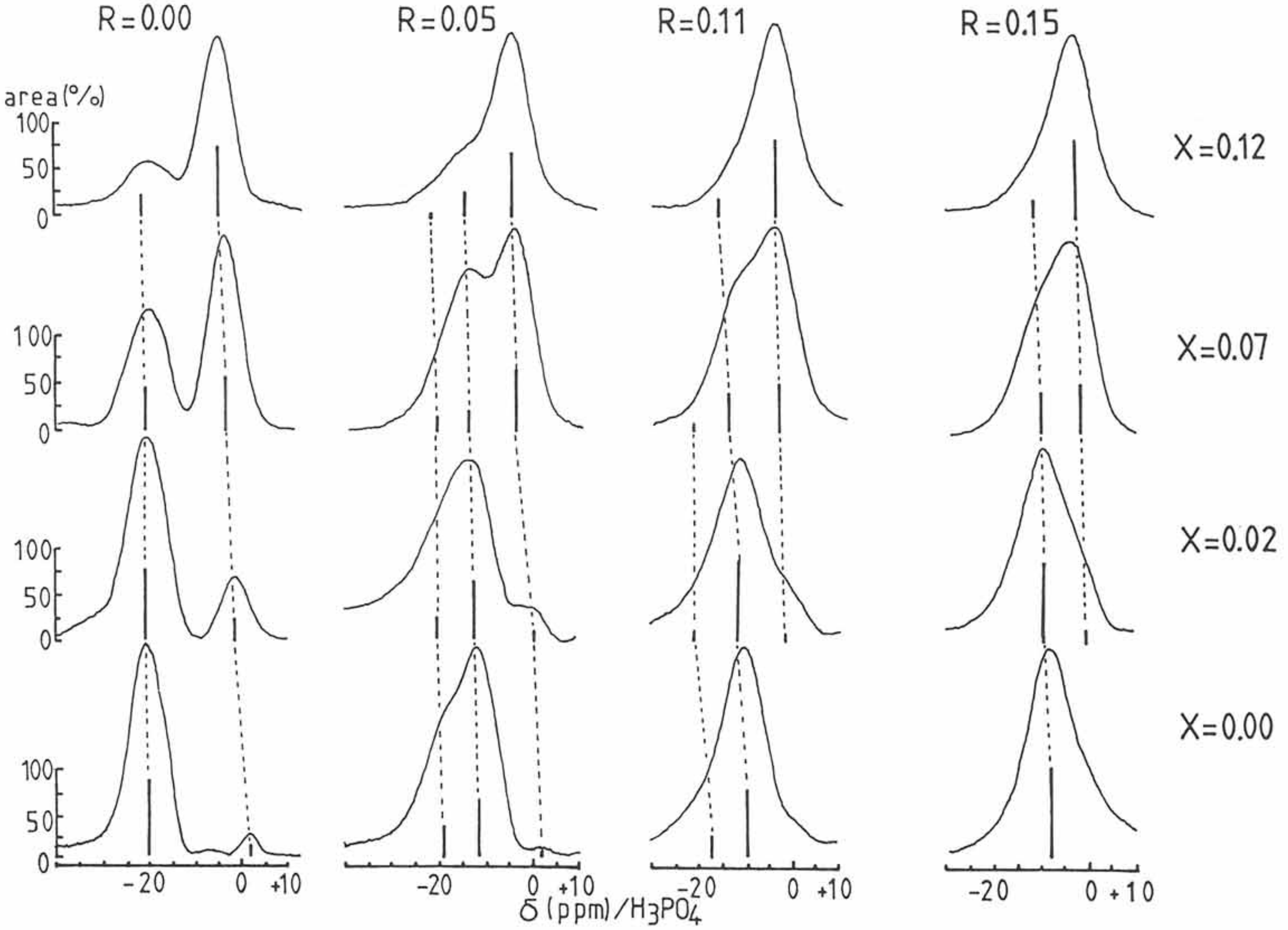
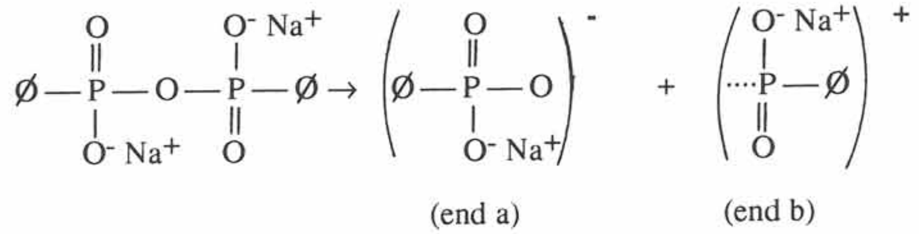
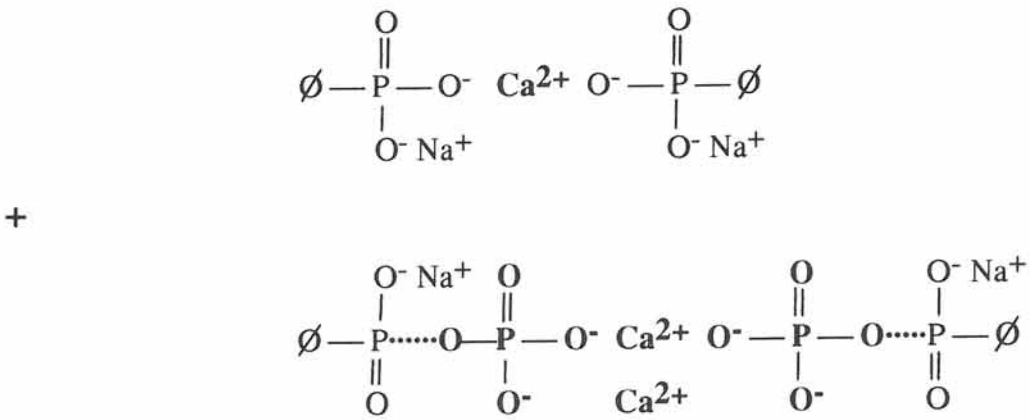


Figure 2-^{31}P MAS NMR spectra (4 KHz) of glasses corresponding to R=0.00, 0.05, 0.11 and 0.15. together with the normalized area values of each deconvoluted resonance band schematized by vertical heavy line.



During the glassy formation, the orthophosphate $[2(PO_4)^{3-}, 3Ca^{2+}]$ units of HAp may react with the a and b end units according to the following scheme:

$$[2(\mathbf{PO_4})^{3-}, 3\mathbf{Ca^{2+}}] + 2\,[\text{end a} + \text{end b}] \rightarrow$$



3-1-2-Sodocalcic borophosphate glasses

The evolution of the ^{31}P MAS NMR spectra as a function of the $Na_2B_4O_7$ content is approximatively similar to the one corresponding to X=0 (Figures 2-4).

At the first introduction of the borate, we notice the appearence of the new resonance line between δ =-14ppm and -11ppm assigned to MB_1 units [2]. For $0.11 \leq R < 0.33$, the shift of this line, towards the lower negative δ, may correspond to the progressive conversion of MB_1 to MB_2 units, in agreement with the previous NMR results [2] (see Table 2). At the same time, the line of MP units disappears. From R=0.33, a new signal occurs at around δ = 0ppm and progressively shifts towards positive values. As in previous ^{31}P NMR study [2], we tentatively identify it with the EB units. For the borate rich-glass samples ($R \geq 10$), the spectra present an additional weak line, between δ =+13ppm and +16ppm which would be assigned to MO units, as previously mentioned in ref. [2].

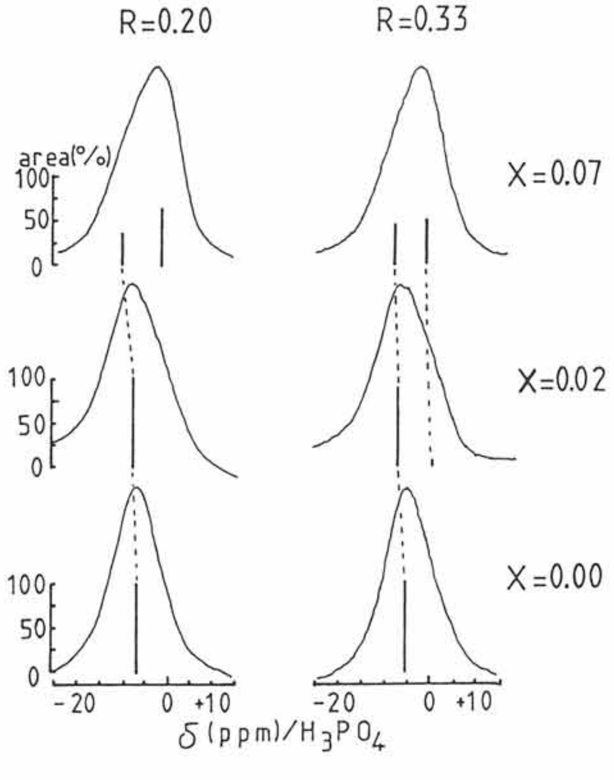


Figure 3-^{31}P MAS NMR spectra (4 KHz) of glasses corresponding to R=0.20 and 0.33 together with the normalized area values of each deconvoluted resonance band schematized by vertical heavy line.

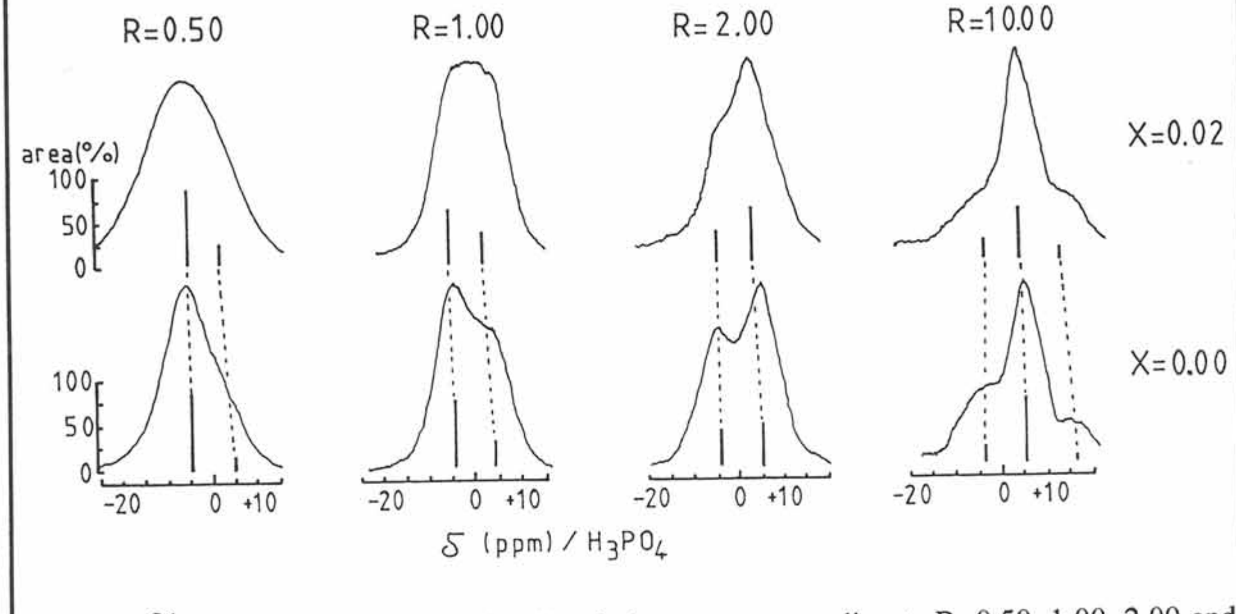


Figure 4-^{31}P MAS NMR spectra (4 KHz)of glasses corresponding to R=0.50, 1.00, 2.00 and 10.00 together with the normalized area values of each deconvoluted resonance band schematized by vertical heavy line.

Generally speaking, the NMR spectra evolution with X, for R constant, shows an increase of EP and / or EB units prejudicial to MP and / or MB units. This means that the shortening of the phosphate chains grows with the addition of HAp. Moreover, the negative shift of the resonance lines seems to show the more and more significant presence of Ca^{2+} cations around the phosphate units as X increases. This is not surprising because the proportion of modifying cations more rapidly rises than the one of forming cations (see values of Ca+Na/B+P ratio in Table 1) with increasing HAp content. The Ca^{2+} cations induce a break of P-O-P and / or P-O-B bridging bonds leading to the formation of more and more end phosphate units. These cations take part in the equalization of charges of non-bridging oxygen atoms and also probably in cross-linkage of the short borophosphate entities. In the borate rich-glass sample (R>0.33, X=0.02), the HAp addition only slightly modify the spectra.

3-2-^{11}B NMR

The ^{11}B NMR spectra selected in Figures 5 (X=0.02) and 6 (R=0.11) are representative of the global evolution of those of the studied glass samples.

The spectra of the glass series, with X=0.02 composition, exhibit an evident change of boron atom environment. As a matter of fact, we recall that the ^{11}B atom, with a nuclear spin equal to 3/2, has an electric quadrupole moment which can strongly interact with the electric field gradient appearing while the boron environment deviates from the cubic symmetry. So, the boron atoms in four- and three-fold coordinations (respectively called B_{IV} and B_{III} subsquently in the text) present two different signals. Then, the central narrow peak is due to B_{IV} atoms, in an environment rather symetrical, which only display a weak electric quadrupole interaction. The broad resonance arises from the electric field gradient produced by the B_{III} atoms in trigonal planar coordination. For more details see ref. [8].

In Figure 5, the spectra consequently show the presence of B_{IV} atoms mainly for weak R values and the two environment types (B_{III} and B_{IV} atoms) for higher borate concentration. A direct measurement of the area under the central peak, with respect of the

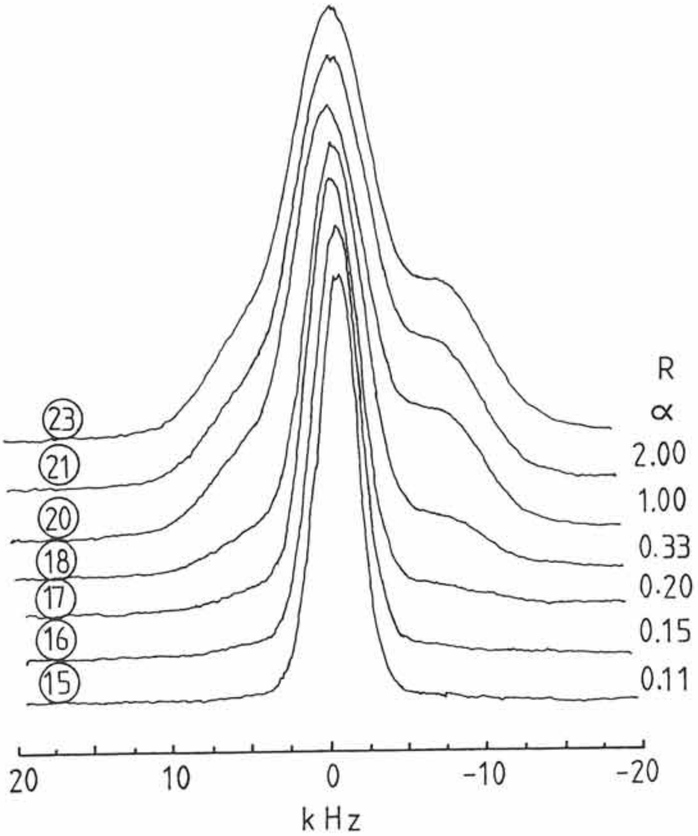


Figure 5-^{11}B NMR spectra of some vitreous samples corresponding to X=0.02.

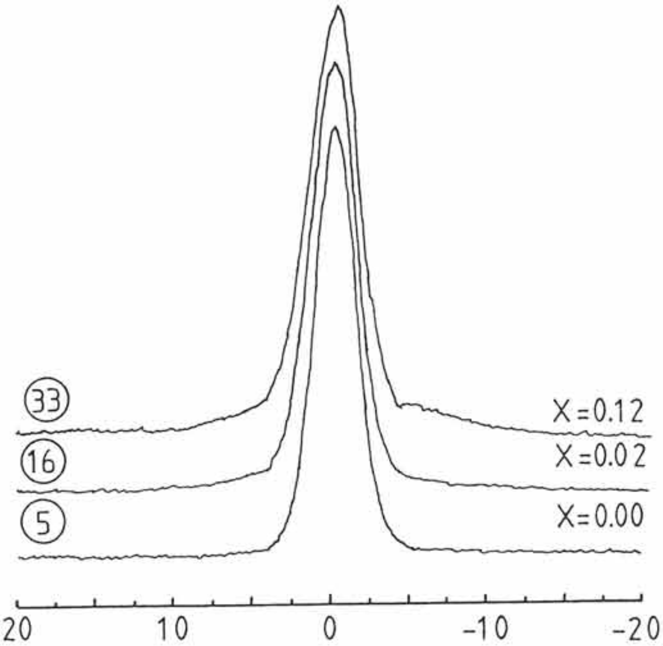


Figure 6-^{11}B NMR spectra of some vitreous samples corresponding to R=0.15.

total area under the entire resonance curve, gives the fraction of B_{IV} atoms. Detailed discussion of this procedure has been published elsewhere by Y. H. Yun et al [9].

B_{IV} atom fraction in relation to the total boron atoms (B_T) has been reported in Figure 7 , for several X values, as a function of the B_T/B_T+P ratio.

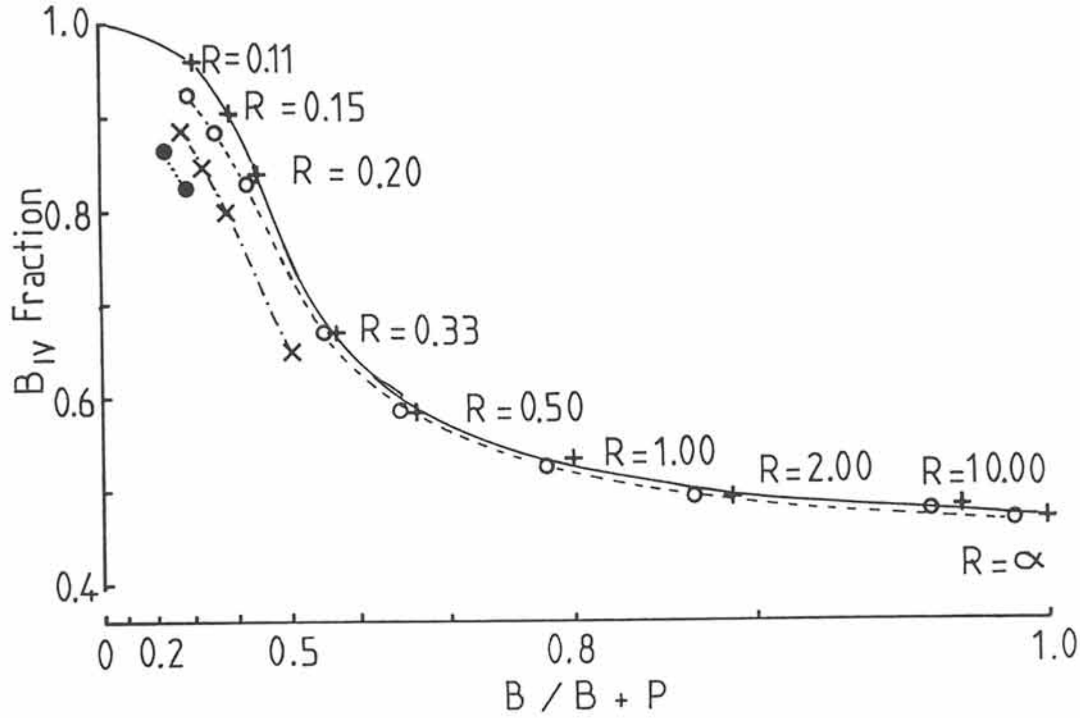


Figure 7-Evolution of B_{IV} fraction as a function of B/B+P ratio for X=0.00 (+), X=0.02 (o), X=0.07 (×) and X=0.12 (•).

In the first addition of the HAp (X=0.02) the B_{IV} atom proportion is virtually unchanged compared to the one found in the pseudo binary glasses (X=0). On the contrary, for the higher HAp content, the corresponding glasses appreciably become poorer in B_{IV} atoms.

This result seems to show that the introduction of HAp interfere with the conversion of B_{III} to B_{IV} atoms. As suggested already, the orthophosphate [2 $(PO_4)^{3-}$, $3Ca^{2+}$] units, forming the HAp structure, could participate to the shortening of the phosphate chains. The B_{IV} atoms perform the similar function but, on the contrary, interconnect these short chains furthering the ramification [6]. Consequently, these two species are competing. If we consider that the bond formation between the end b (see above) and $(PO_4)^{3-}$ of HAp is easier (thermodynamically more stable) than the P-O-B_{IV}-O-P bond formation (including the conversion of B_{III} atoms to B_{IV} atoms), we understand that the B_{IV} fraction is weaker in the sodocalcic borophosphate glasses than in those without HAp.

4-CONCLUSIONS

^{31}P MAS and ^{11}B NMR have been used for structural investigations on the glass samples having the following chemical composition (1-X) $[NaPO_3+R\ Na_2B_4O_7]+X\ Ca_5(PO_4)_3OH$.

Generally speaking, the addition of $Ca_5(PO_4)_3OH$ in the borophosphate glasses induces a significant "depolymerization "of the borophosphate glass former network.

For R=0, starting from the pure metaphosphate vitreous $NaPO_3$ (X=0) made of finite $(O_2PO_{2/2})_n{}^{n-}$ chains (n=20), the introduction of HAp produces a shortening of the length of phosphate chains, leading to the devitrification for X close to 0.14, with the formation of $[(O_{1/2}PO_3)^{2-}, Na^+, 0.5Ca^{2+}]$ and $[(O_{1/2}PO_3)^{2-}, Ca^{2+}]$ chain ends.

In the sodocalcic borophosphate glasses with the borate-poor concentration ($0<R\leq0.2$), the $BO_{4/2}{}^-$ formed, numerically smaller than in sodium borophosphate glasses, are used as branching units between short phosphate chains with probably a strong tendency of random ramification which contributes to preserve the vitreous domain. As in the borophosphate glasses previously studied [2-4], the major part of the $BO_{4/2}{}^-$ units are probably compensated by phosphate units, leading to the formation of borophosphate groups of the form: $BOPO_2{}^{2-}OP$ and $BOPO_2{}^-OP$ (MB_1) and then $BOPO_2{}^{2-}OB$ and $BOPO_2{}^-OB$ (MB_2). The boron atoms in triangular coordination may be connected to the phosphate units as in the sodium borophosphate glasses (X=0).

On the contrary, in the borate rich concentration range (R>0.5), the quasi totality of B_{IV} atoms with the B_{III} atoms, are probably inserted in the borate cycles and consequently cannot balance the break effect of the HAp addition leading to the formation of a very narrow glassy domain.

The depolymerization of the borophosphate former network, following the break and the shortening of the phosphate chains, can be correlated to the evolution of the physical and chemical properties, such as the decrease of the glass forming ability (Tc-Tg) and the compactness. On the contrary, the cross-linkage of the short borophosphate groups by the Ca^{2+} cations might be at the origin of the strengthening of the microhardness and the insolubility of these glasses in water.

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B-2-ETUDE PAR DIFFUSION RAMAN

A partir des résultats de RMN (^{31}P MAS et ^{11}B), nous renseignant sur l'environnement immédiat des atomes de bore et de phosphore, quelques hypothèses ont pu être formulées sur la structure des verres de composition (1-X) [$NaPO_3$-R $Na_2B_4O_7$]-X $Ca_5(PO_4)_3OH$, en fonction de X.

D'une façon générale, l'introduction d'apatite dans les verres borophosphatés de sodium provoque une dépolymérisation du réseau formateur.

Dans le cas des verres phosphatés sodocalciques (R=0), la présence accrue d'apatite conduit à une diminution de la longueur moyenne des chaines métaphosphates, dont les terminaisons sont formées d'unités [$(O_{1/2}PO_3)^{2-}$, Na^+, 0.5 Ca^{2+}] et [$(O_{1/2}PO_3)^{2-}$, Ca^{2+}].

Ce phénomène se produit également pour les verres borophosphatés sodocalciques au détriment des liaisons BOP. Le bore, principalement tétracoordiné réticule des chaînons phosphatés de plus en plus courts jusqu'à R voisin de 0,2.

Pour des valeurs de R>0.5, la faible possibilité d'addition d'hydroxyapatite (X=0,02) conduit à des verres de structure analogue à celle des compositions où X=0.

Comme pour les verres borophosphatés de sodium et pour les mêmes raisons, une étude par spectroscopie Raman a été entreprise.

Soumis à *Journal of Non-Crystalline Solids*

INFLUENCE OF THE ADDITIONAL CALCIUM-HYDROXYAPATITE ON SODIUM BOROPHOSPHATE GLASSES.

PART II: RAMAN INVESTIGATIONS.

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Abstract

A structural study by Raman spectroscopy of the series of glasses with compositions (1-X) ($NaPO_3$ - R $Na_2B_4O_7$) -X $Ca_5(PO_4)_3OH$ has been carried out. In conjonction with previous vibrational results (IR and Raman) of glasses with compositions (1-x) $NaPO_3$ -x $Na_2B_4O_7$, a structural approach can be proposed as a function of X. The introduction of hydroxyapatite in the vitreous $NaPO_3$ (R=0) produces a shortening of the length of phosphate chains, leading to the formation of $(O_{1/2}PO_3)^{2-}$ chain ends "cross-linked" by Ca^{2+} cations. In the borophosphate glasses (borate poor-compositions), the break effect of hydroxyapatite addition is preferably located in the POP bridges with also a "cross-linking" of the borophosphate groups by Ca^{2+} cations. Nevertheless, breaks of BOP bridges could be also considered, in the range of the borate rich-compositions. The "depolymerization" effect of the addition of the hydroxyapatite has been correlated to the evolution of the physical and the chemical properties.

1-INTRODUCTION

In a previous paper [1], the effect of addition of the calcium hydroxyapatite $Ca_5(PO_4)_3OH$ (called HAp subsequently in the text), known for its role in mineralization of the living hard tissus, in the $NaPO_3$ - $Na_2B_4O_7$ system has been studied. The physical and chemical characterizations of glass samples, stemed from the vitreous domain in $NaPO_3$ - $Na_2B_4O_7$ - $Ca_5(PO_4)_3OH$, have shown changes of most of the studied properties such as increase of the glass transition and crystallization temperatures, strengthening of microhardness and water resistance, compared with the sodium borophosphate glasses [2].

A recent ^{31}P MAS NMR and ^{11}B NMR study [3], has shown that the addition of HAp in (1-x) $NaPO_3$ - x $Na_2B_4O_7$ compositional glasses induces a significant "depolymerization" of the sodium borophosphate ramified network [4], leading to the formation of the short borophosphate groups ended by $O_{1/2}PO_3^{2-}$ units probably "cross - linked" by Ca^{2+} cations.

This paper is devoted to the structural investigation of series of glasses with compositions (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ (R=x/1-x, x corresponding to the fraction of $Na_2B_4O_7$ in the pseudo binary system (1-x) $NaPO_3$ - x $Na_2B_4O_7$) by mean of Raman scattering experiments. The goal will be to identify the borophosphate groups formed and its interconnections as a function of the HAp content. The interpretation of Raman data will be based on the previous Raman results for the sodium borophosphate glasses [5].

2-EXPERIMENTAL DETAILS.

Glasses with composition (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ have been prepared as described previously [1]. They stem from the vitreous domain of the $NaPO_3$ - $Na_2B_4O_7$ - $Ca_5(PO_4)_3OH$ pseudo ternary system (Figure 1) [1]. The compositions of the most representative glass samples studied in this work (X and R values) together with the corresponding B/B+P and Na+Ca/B+P ratio values are reported in Table 1.

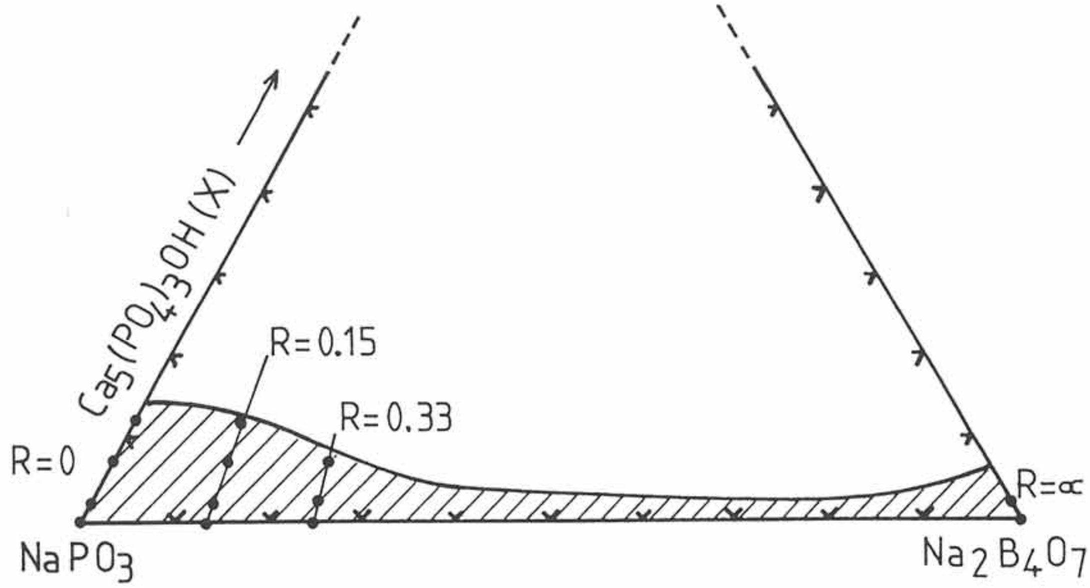

Figure 1: Vitreous domain (hatched area) and glass samples studied (black point) corresponding to the composition (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$.

X\R	**0**	**0.15**	**0.33**	∝
0	0 ***1*** 1	0.374 ***5*** 0.813	0.571 ***7*** 0.714	1.000 ***12*** 0.500
0.02	0 ***13*** 1.038	0.358 ***16*** 0.849	0.552 ***18*** 0.746	0.985 ***23*** 0.518
0.07	0 ***24*** 1.123	0.322 ***27*** 0.932	0.506 ***29*** 0.823	
0.12	0 ***30*** 1.194	0.289 ***33*** 1.007		

Table-1: Composition (X and R values), B/B+P and Na+Ca/B+P ratio values corresponding to the glass samples (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ studied by Raman scattering.

0.374 ← B/B+P
5 ← Sample number
0.813 ← Na+Ca/B+P

The Raman spectra have been recorded on a Dilor Z 24 triple - monochromator instrument, coupled with an argon ion laser Spectra - Physics model 171; a cooled Hamamatsu photomultiplier coupled with a photon - counting system was used for detection. The colourless glass samples have been cut in shape of parallelepipeds of dimensions about 10 x 10 x 10 mm^3 and with surface carefully polished. Right angle scattering geometries have been adopted with parallel (VV) and perpendicular (VH) polarizations of incident and scattered beams. The 514.5 nm argon emission line has been used for excitation, with incident powers ranging from 100 to 300 mW; the spectral resolution was of about 2.5 cm^{-1}.

3-RESULTS AND DISCUSSION

The parallel (VV) polarized Raman spectra of the most representative (1-X) [$NaPO_3$-R $Na_2B_4O_7$]-X $Ca_5(PO_4)_3OH$ compositional glass samples are reported in Figures 2 (R=0), 3 (R=0.15), 4 (R=0.33) and 5 (R=∝).

For comparison, the Raman spectra of crystalline HAp [6], $M_{3/m}{}^{m+}(PO_4)^{3-}$ [7, 11] and $M_{4/m}{}^{m+}(P_2O_7)^{4-}$ [8, 11-15] and vitreous $M_{5/m}{}^{m+}(P_3O_{10})^{5-}$ [7, 9-15], $M_{6/m}{}^{m+}(P_4O_{13})^{6-}$ [7, 9, 10, 11, 14, 15] and $M_{1/m}{}^{m+}(PO_3)^{-}$ [10, 11, 13-15,] [M=Na (m=1) or Ca (m=2)] are schematized in Figure 6.

The Raman data for the glass samples corresponding to X=0 ($NaPO_3$-R $Na_2B_4O_7$) have shown the existence of the usual vibrational modes such as νPO_2, νPOP, νPO_3 and νPO_4 of middle $POPO_2^-OP$ (MP), end $POPO_3^{2-}$ (EP) and monomeric PO_4^{3-} (MO) phosphate units and also typical modes corresponding to borophosphate groups (boron-bonded middle phosphate units) [5]. The addition of $Na_2B_4O_7$ up to R=0.25 induces a shortening of the metaphosphate chains length. From ^{11}B NMR results, we know that the boron atoms mainly are under the $B_{IV}O_{4/2}^-$ form which is either compensated by Na^+ cation or by the phosphate unit [3]; in this last case the boron and the phosphorus have been respectivelly called B_c and P_c. The borate groups are used as branching units between small phosphate chains, with a tendency of network ramification, resulting in the formation of borophosphate groups such as: $(O_{3/2}B_{IV}OPO_{5/2})^-$, $(O_{3/2}B_{cIV}OP_cO_{5/2})^{2-}$ and

FREQUENCY	ASSIGNMENT
Phosphate vibration modes	
1270 - 1210 cm-1	$\nu P_cO^-$and / or $\nu P{=}O$ and / or $\nu_{as}PO_2$
1165 - 1120 cm^{-1}	ν_sPO_2 in MP chain then MB_1 unit
$1120\ cm^{-1}$ / $1100\ cm^{-1}$	ν_sPO_2 in MB_2 unit with two B_{IV} ν_sPO_2 in MB_2 unit with one B_{IV} and one B_{III} or two B_{III}
1070 - 1085 cm^{-1}	$\nu_sP_cO_2$ in MB_1 unit with one B_{IV}
$1040\ cm^{-1}$ / $990\ cm^{-1}$ / $985\ cm^{-1}$	$\nu_sP_cO_2$ in MB_2 unit with two B_{IV} $\nu_sP_cO_2$ in MB_2 unit with one B_{III} and one B_{IV} ν_sPO_3 in EB and / or ν_sPO_4 in MO unit
$1015\ cm^{-1}$	ν_sPO_3 in EP
Borophosphate vibration modes	
$760\ cm^{-1}$	ν_sP_c-O-P in MB_1 unit
720 - 715 cm^{-1}	ν_sP_c-O-B_c in MB_1 then MB_2 units
685 - 695 cm^{-1}	ν_sP-O-P in MP then MB_1 units
640 - 625 cm^{-1}	ν_sP-O-B in MB_1 then MB_2 units
Borate vibration modes	
1345 - 1385 cm^{-1}	ν_sBO^-
$975\ cm^{-1}$	not well established (existence in pure borate)
$765\ cm^{-1}$	ν"Breathing" of borate cycles (di - penta, ditri, tri and di - borate groups)
$500\ cm^-$	νBOB out side borate cycles (not well established)

Table-2:Tentative assignments and positions of various phosphate, borophosphate and borate vibration modes in $NaPO_3$ - R $Na_2B_4O_7$ vitreous composition [4, 5].

$(O_{3/2}B_{cIV}OP_cO_{4/2})^-$. In the borate rich concentration range ($0.25 \leq R \leq \infty$), six - membered borate rings including B_{IV} and B_{III} atoms such as those found in pure vitreous $Na_2B_4O_7$, are present. The phosphate units, which of course progressively disappear as R increases, bridge the borate groups. For the lower phosphate concentrations (i.e. $R \approx 10$), $O_3PO_{1/2}{}^{2-}$ end units connected to the borate groups and $PO_4{}^{3-}$ isolated monomers may be present in the glass. The assignments and the positions of phosphate, borophosphate and borate vibration modes are summarized in Table 2. For more detail see ref.[4, 5].

3-1-Sodocalcic phosphate glasses (R=0).

Let us first examine the Raman spectrum of the pure phosphate glass $NaPO_3$ (sample 1; Figure 2). This spectrum (VV) is dominated by two strong lines situated at 1164 (line (a)) and 685 cm^{-1} (line (g)), assigned respectively to the symmetric stretching modes ν_s (PO_2) and ν_s (POP) of quasi infinite metaphosphate chains $(O_2PO_{2/2})_n{}^{n-}$ [14]; a weak line at 1269 cm^{-1} and a broad band at ~ 940 cm^{-1} correspond to the antisymmetric stretching modes ν_{as} (PO_2) and ν_{as} (POP), respectively. Moreover, there is an additional weak line at 1016 cm^{-1} (line (n)) that we assign to the symmetric stretching mode ν_s (PO_3) of $O_3PO_{1/2}{}^{2-}$ end units in agreement with ^{31}P NMR experiments where a small amount of such end groups has been evidenced in vitreous $NaPO_3$ [16]. This means that the phosphate chains have finite lengths ($n \approx 20$ in average); as a consequence, for charge compensation, a few "neutral" $O{=}PO_{3/2}$ (as much as $O_3PO_{1/2}{}^{2-}$ ends) branching different chains may be present and, if such was the case, the characteristic ν (P=O) frequency of these groups could be superimposed on the weak ν_{as} (PO_2) line at 1269 cm^{-1}(line (m)), as found in ultraphosphates [17].

At the first addition of HAp (Figure 2, sample 13), we notice the appearence of new shoulders (o) (~ 1100 cm^{-1}), (p) (~ 990 cm^{-1}) and (q) (~ 730 cm^{-1}) respectively in the ν_s (PO_2) or ν_{as}(PO_3) and ν (POP) frequency ranges. As the HAp concentration increases, we observe an intensity increase of these lines together with that of line (n), and conversely, a progressive intensity decrease of the lines (m), (a) and (g) with a shift for the two first lines

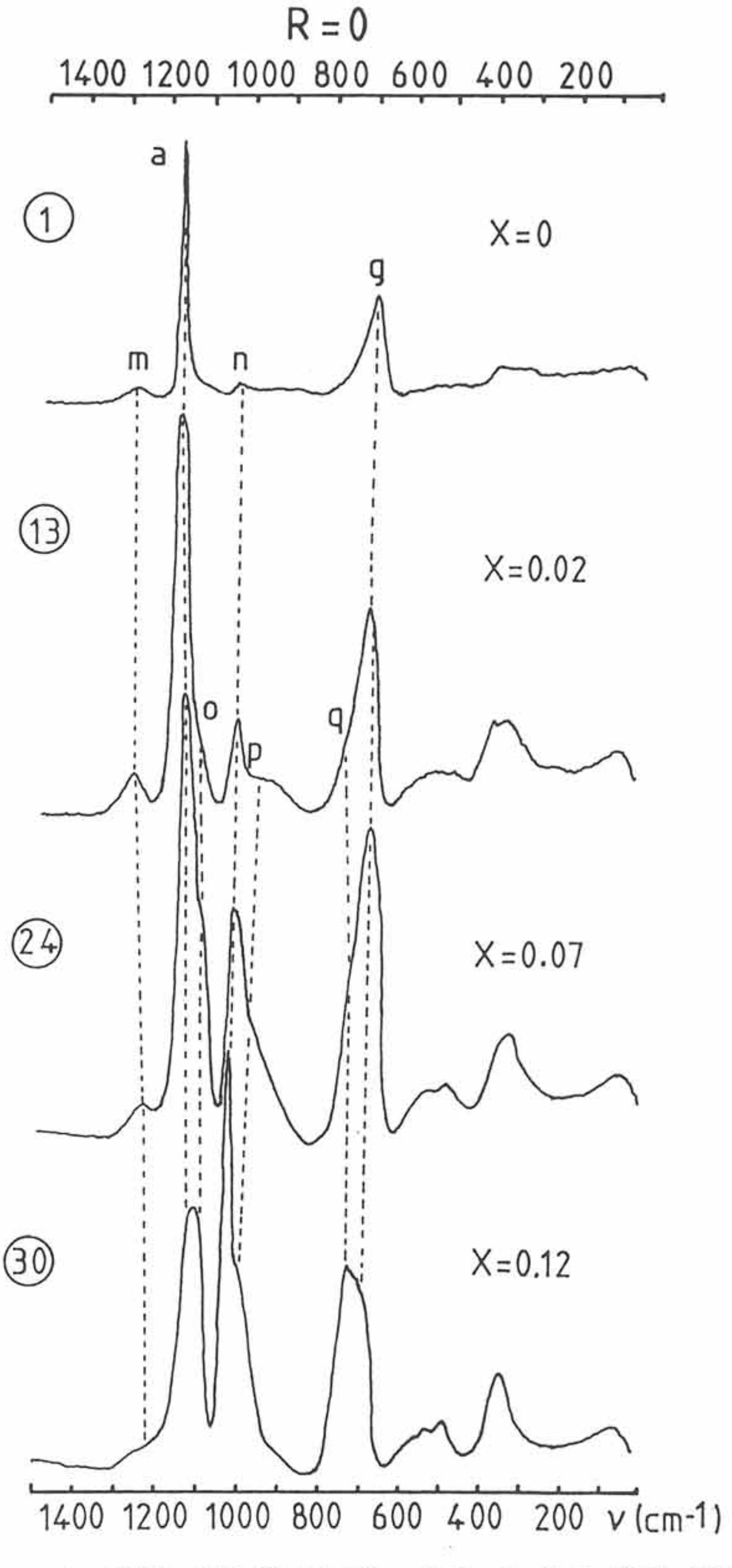

Figure 2: Raman spectra (VV) of (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ glass samples with R=0 (1, 13, 24 and 30; see Table 1)

(~ 1250 cm^{-1}; ~ 1120 cm^{-1}). By comparison with the Raman spectra of the reference compounds (figure 6), we conclude that a progressive shortening of the metaphosphate chains lenght occours as X increases.The spectrum of the sample 30 (X=0.12) is very close to those of the $M_{5/m}{}^{m+}(P_3O_{10})^{5-}$ and $M_{6/m}{}^{m+}(P_4O_{13})^{6-}$ glasses (Figure 6). The lines (o) and (n) may be respectively assigned to ν_{as} and ν_s (PO_3) and (p), (q) and (g) to ν_{as} and ν_s (POP). These results are in perfect agreement with the previous ^{31}P MAS NMR study in which a breaking mechanism of the phosphate chains, during the glass formation, has been suggested according which $O_{1/2}PO_3{}^{2-}$ chain ends "cross-linked" by Ca^{2+} cations take place [3].

3-2-Sodocalcic borophosphate glasses

3-2-1-R=0.15

The introduction of $Na_2B_4O_7$, without HAp, induces a progressive shortening of the metaphosphate chains lenght [4, 5]. The borate groups, mainly in the $B_{IV}O_{4/2}{}^-$ form are used as branching units between the small phosphate chains, producing a tendency of random ramification of the glass network. In the Raman spectrum (Figure 3; sample 5), this effect is evidenced by the emergency of the new lines (b), (c) and (d) in the ν (PO_2) frequency range and lines (e), (f) and (h) in the ν (POP and / or POB) frequency range which are assigned, as mentioned in Table 2 [4-5].

The HAp addition provokes modifications of the Raman spectra (see Figure 3). The intensity of the lines (m), (a) and (g) corresponding respectively to ν_{as} (PO_2), ν_s (PO_2) and ν_s (POP) in the MP chains and the lines (c) and (e) corresponding to ν_s (P_cO_2) and ν_s (P_cOP) in $B_{cIV}OP_cO_{3/2}{}^-OP$ and / or $B_{cIV}OP_cO_{4/2}{}^{2-}OP$ units (MB_1) (Table 2) decreases as X increases. For X=0.12, the spectrum exhibits an exalted line (d) corresponding to ν_s (P_cO_2) in $B_{cIV}OP_cO_{4/2}{}^{2-}OB$ units (MB_2), the persistence of lines (b), (f) and (h) respectively assigned to ν_s (PO_2) , ν_s (P_cOB_c) and ν_s (POB) modes in MB_1 and/or MB_2 units (Table 2) and finally the presence of new lines : (r) around 1000 cm^{-1} and (s) around 970cm^{-1} in the ν_s (PO_3) and ν_s (PO_4) frequency ranges. The line (r) may be assigned to ν_s (PO_3) vibration

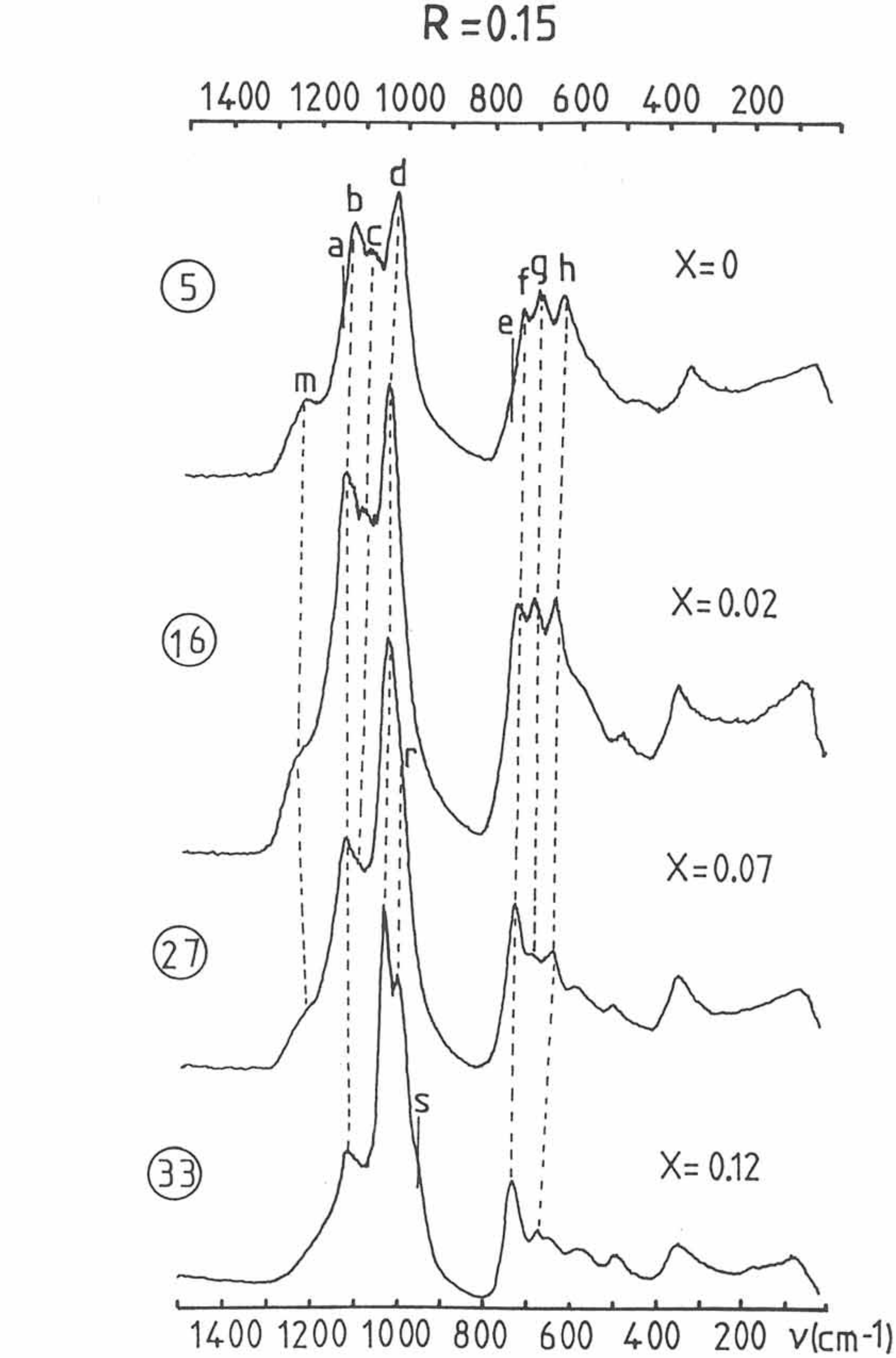

Figure 3: Raman spectra (VV) of (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ glass samples with R=0.15 (5, 16, 27 and 33; see Table 1)

mode of short phosphate and / or borophosphate chains as the line (n) mentioned above (Figure 2). According to NMR results [3], the assignment of the shoulder (s) to ν_s (PO_4) vibration mode seems to be ruled out. So, this line should result either from a new ν_s (PO_3) vibration mode or more probably from ν_{as} (POB) antisymetric vibration mode.

We conclude to a depolymerization of the random ramified borophosphate glass network.

The desappearence of the line (e) (ν_s (P_cOP)) and (g) (ν_s (POP)) and the persistency of the line (f) (ν_s (P_cOB_c)), as X increases, seem to show that the break of the borophosphate chains is mainly located in the POP bridges with the formation of the $O_{1/2}PO_3{}^{2-}$ phosphate ends such as EP or EB ($BOPO_3{}^{2-}$) units. Nevertheless, the break of the BOP bridges cannot be ruled out. As the matter of fact, the intensity of the line (h) decreases as X increases. Moreover, ^{11}B NMR study [3] shows that the HAp addition induces a decrease of the proportion of boron atoms in four -fold coordination (0.91 for X=0 and 0.82 for X=0.12), so, the break of POB bridges could possibly lead to the formation of the additional boron atoms in the three-fold coordination but such a mechanism cannot be early established.

3-2-2-R=0.33

The spectrum of the glass sample 7 (Figure 4) consists of lines (m), (b), (d), (f) and (h) mentionned above with new lines (l) and (i) corresponding respectively to ν BO^- and ν "breathing" of borate cycles (Table 2) [4, 5]. In this glass, six - membered borates rings, including boron atoms in three and four - fold coordinations such as found in pure vitreous $Na_2B_4O_7$ are present, together with B-O bonds with non - bridging oxygens atoms. The phosphate units in the form of MB_2 units bridge the borate groups.

The addition of HAp (samples 18 and 29, Figure 4) simultaneously induce a progressive intensity decrease of the lines (m), (b) and (f). On the other hand, the line (d) splits with an exaltation of the component located in a rather frequency low range for PO_2 stretch modes. Consequently, this latter component could be assigned to ν_s (PO_3) of $O_{1/2}PO_3{}^{2-}$ end units connected to borate rings. We note that the intensity of the line (i) and (l), characteristic of the borate cycles decreases as X increases. This behavior is not surprising because the X increase corresponds to a decrease of the B/B+P ratio, reaching the value of 0.5 for the sample 29, thus inducing a decrease of borate groups in the glass network. As mentionned already (R=0.15), the HAp addition leads to the break the BOP bridges (line (h)) with the formation of the phosphate end units and the depolymarization of the borophosphate network.

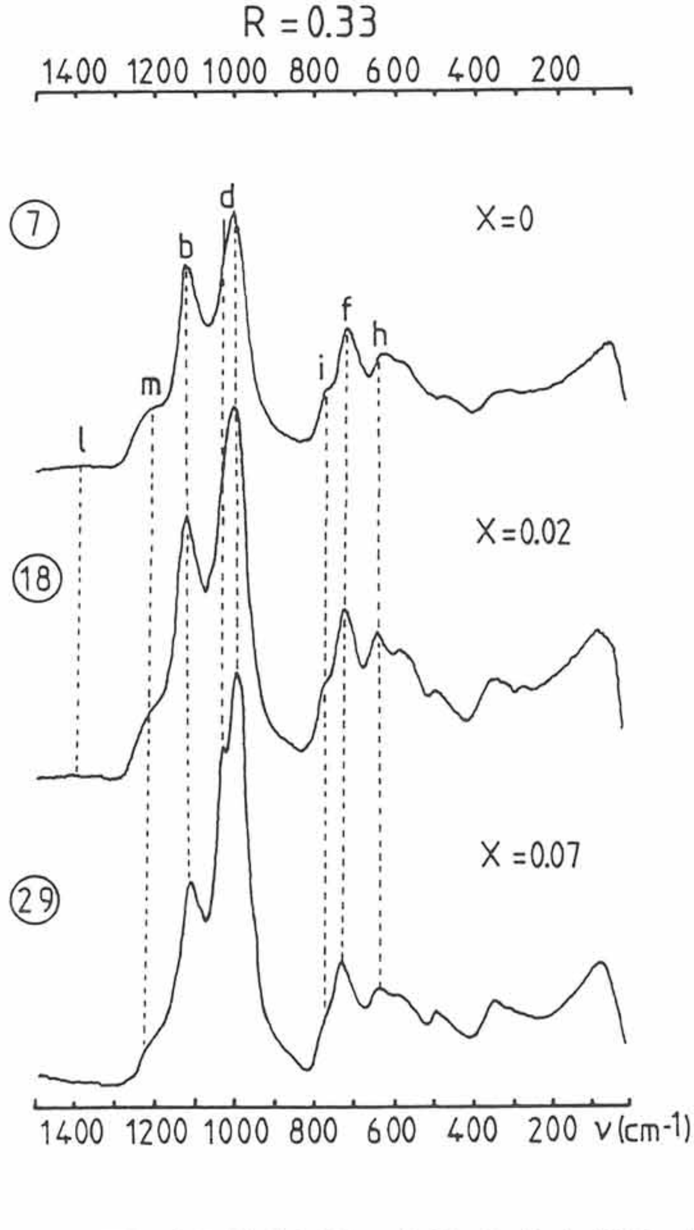

Figure 4: Raman spectra (VV) of (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ glass samples with R=0.33 (7, 18 and 29; see Table 1)

3-2-3-R=∝

Introduction of HAp in the borate glass (sample 23, Figure 5) induces a new line (t) emerging around 950 cm^{-1}. The new line could be assigned to the ν_s (PO_3) of $O_3PO_{1/2}{}^{2-}$ end units connected to a borate ring or, more probably, to the symmetric stretch of isolated $PO_4{}^{3-}$ monomers in accordance with the spectra of crystalline $M_{3/m}{}^{m+}(PO_4)^{3-}$ (Figure 6) and the study of baryum borophosphate glasses [18].

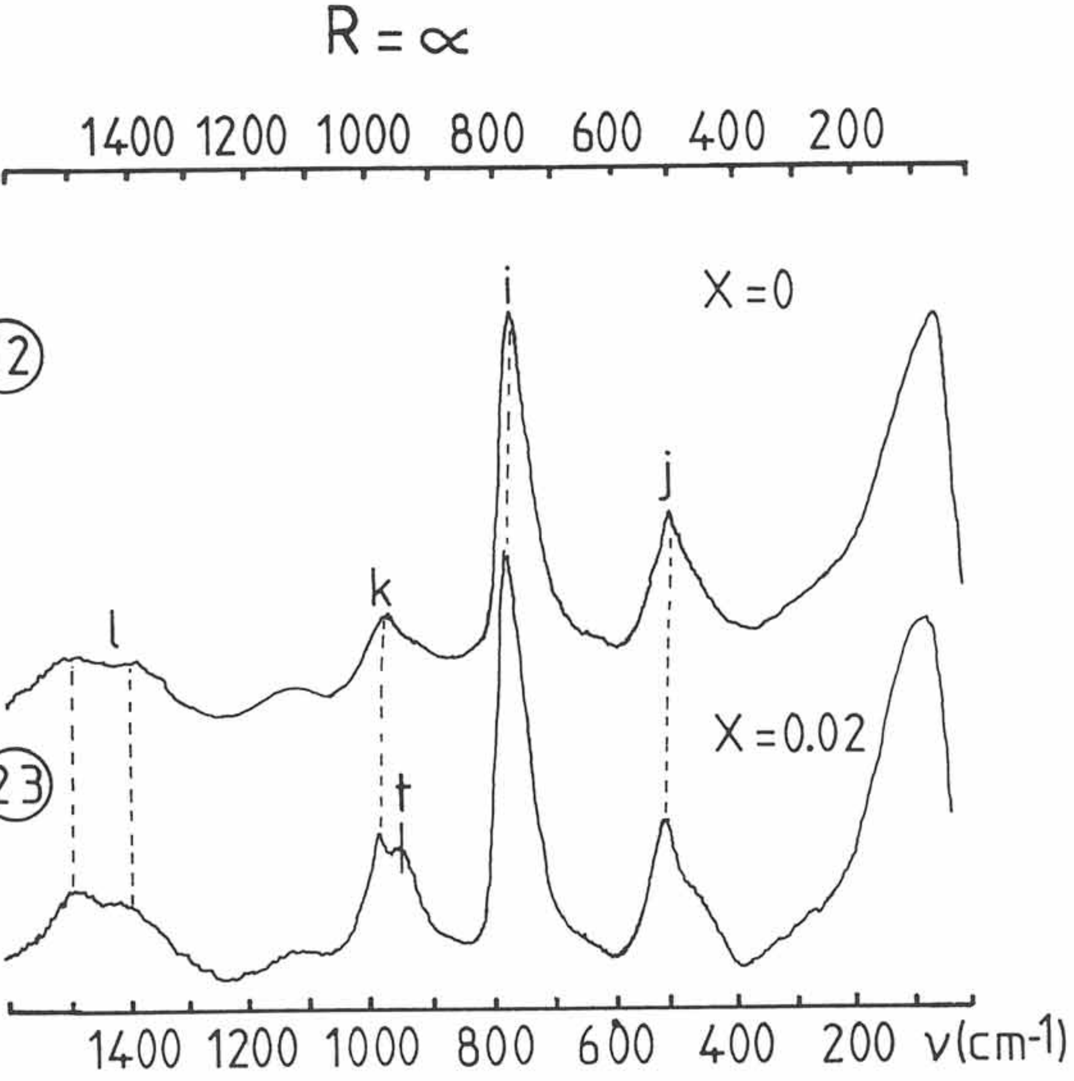

Figure 5: Raman spectra (VV) of (1-X) [$NaPO_3$ - R $Na_2B_4O_7$] - X $Ca_5(PO_4)_3OH$ glass samples with R=∝ (12 and 23; see Table 1)

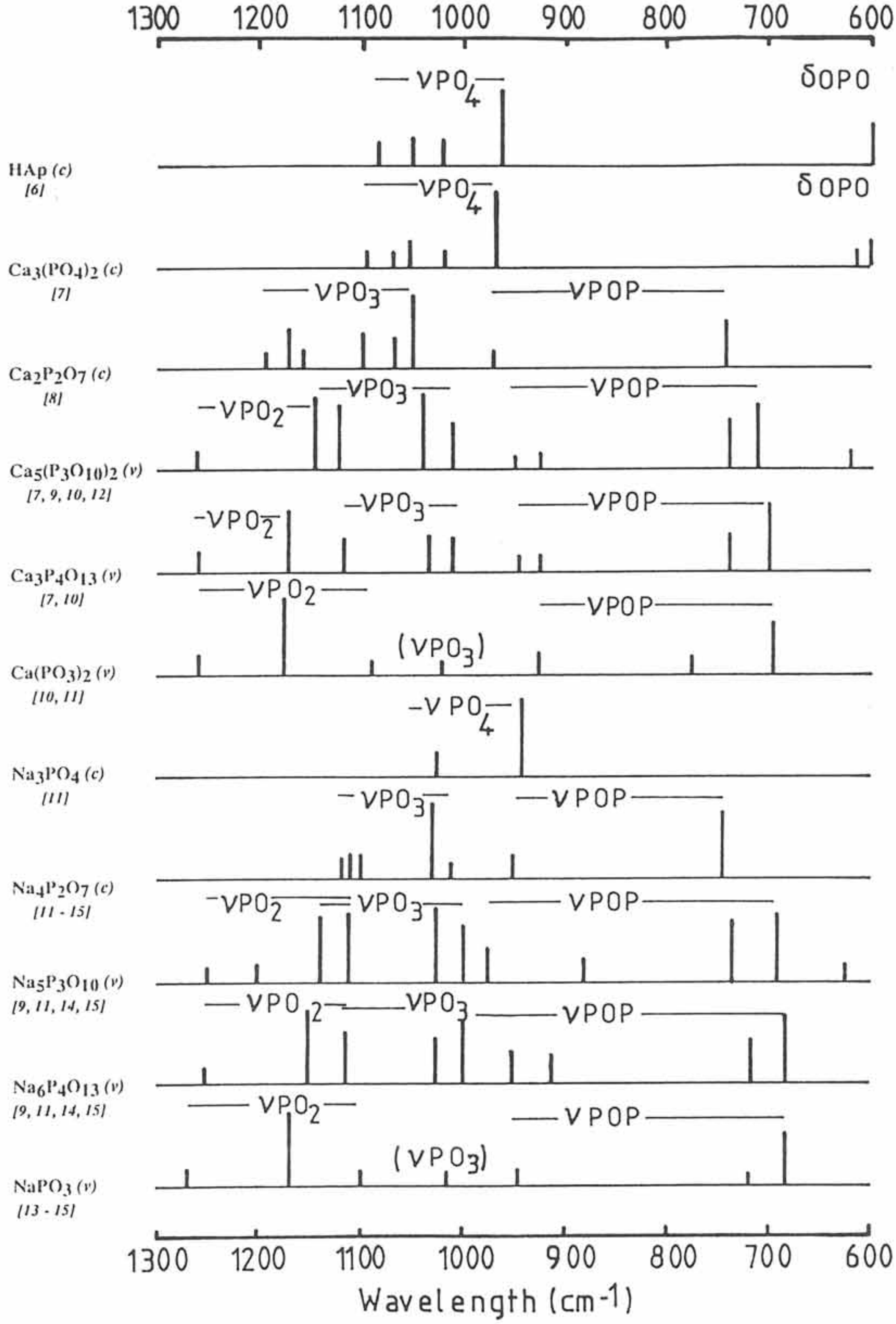

Figure 6: Schematic Raman spectra of crystalline (c) HAp [6], $M_{3/m}{}^{m+}(PO_4)^{3-}$ [7, 11] and $M_{4/m}{}^{m+}(P_2O_7)^{4-}$ [8, 11- 15] and vitreous (v) $M_{5/m}{}^{m+}(P_3O_{10})^{5-}$ [7, 9-15], $M_{6/m}{}^{m+}(P_4O_{13})^{6-}$ [7, 9, 10, 11, 14, 15] and $M_{1/m}{}^{m+}(PO_3)^{-}$ [10, 11, 13-15,] [M=Na (m=1) or Ca (m=2)].

4-CONCLUSIONS

Raman scattering study of the $(1\text{-}X)\ [NaPO_3 - R\ Na_2B_4O_7] - X\ Ca_5(PO_4)_3OH$ compositional glasses, in conjonction with NMR results obtained previouly [3], made it possible to propose a structural approach, as a function of the additional HAp (X).

For R=0, starting from the pure metaphosphate vitreous $NaPO_3$ (X=0) made of quasi infinite $(O_2PO_{2/2})_n^{n-}$ chains (n=20), the introduction of HAp produces a shortening of the length of phosphate chains, leading to the formation of $(O_{1/2}PO_3)^{2-}$ chain ends "cross-linked" by Ca^{2+} cations. The HAp richer glasses are built up from an association of $(P_3O_{10})^{5-}$ and / or $(P_4O_{13})^{6-}$phosphate groups.

In the borate poor - compositional range, the $BO_{4/2}^-$ units are compensated mainly by phosphate units, as in sodium borophosphate glasses, thus contributing to a random ramification of the glass network. The HAp addition induces breaks located preferably on the POP and P_cOP bridges in the phosphate chains (as in the sodocalcic phosphate), and in $B_{cIV}OP_cO_{3/2}^-OP$ and / or $B_{cIV}OP_cO_{4/2}^{2-}OP$ borophosphate units, with the formation of $O_{1/2}PO_3^{2-}$ end groups, probably "cross - linked" by Ca^{2+} cations. Nevertheless, breaks of BOP bridges could be also considered correlated with the formation of additional boron atoms in three - fold coordination.

In the borate rich - compositions of the borophosphate glasses, the phosphate units, in small number, bridge the borate cycles made of borons atoms in four - and three - fold coordination, as found in pure vitreous $Na_2B_4O_7$. The break effect of HAp addition, mainly located in the BOP bridges, provokes a strong "depolymerization" leading to the existence of a very narrow glassy domain along the $NaPO_3$ - $Na_2B_4O_7$ pseudo binary system.

In the pure borate glasses the additional HAp happen in form of isolated PO_4^{3-} monomers.

Generally speaking, the break of the borophosphate network can be correlated to the evolution of the physical and chemical properties, such as the decrease of the glass forming ability (Tc-Tg) and consequently the narrow vitreous domain and compactness. In contrast, the "cross-linkage" of borophosphate groups by the Ca^{2+} cations might be at the origin of the strengthening of the microhardness and the insolubility of these glasses in water.

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CHAPITRE III

MISE AU POINT D'UN PROCEDE DE RESTAURATION DENTAIRE

INTRODUCTION DU CHAPITRE III

Dans le chapitre précédent nous avons pu montré que l'introduction d'hydroxyapatite dans les verres à fort pouvoir vitrifiant de composition (1-x) $NaPO_3$ - x $Na_2B_4O_7$ entrainait une dépolymérisation du réseau borophosphaté, tout en maintenant une cohésion importante entre les groupements formés, due à la présence d'ions Ca^{2+}.

Ces deux effets antagonistes se traduisent par une augmentation de la dureté ($Hv \leq 460$ $daN.mm^{-2}$) et de la résistance à l'eau ($S \leq 10^{-10}$ $g.cm^{-2}.mn^{-1}$) tout en conservant des températures de transition vitreuse modérées ($Tg \leq 530°C$).

Ces caractéristiques physico-chimiques semblaient faire, a priori, de ces matériaux de bons candidats à la restauration dentaire pouvant être fondus in situ, sous l'action d'un faisceau laser CO_2 ($\lambda = 10,6 \mu m$).

L'étude qui suit concerne la recherche d'un procédé d'obturation de caries dentaires. Elle retrace successivement les contraintes liées au choix des matériaux utilisables, les essais d'obturation, le comportement thermique au cours d'un traitement et enfin, la proposition d'un procédé.

Le but de ce travail était de rechercher des matériaux de restauration dentaire pouvant être fondus, in situ, sous l'action d'un faisceau laser CO_2: (λ = 10,6 µm). Cette étude a été aidée financièrement par SATELEC, filiale de SANOFI (groupe ELF AQUITAINE) et par la REGION AQUITAINE.

A-CHOIX DES MATERIAUX

Les matériaux choisis devraient, dans tous les cas, posséder une bonne adhésion avec les tissus dentaires et satisfaire aux critères suivants :

-absorption importante à la longueur d'onde du faisceau incident (laser CO_2: ν=943 cm^{-1})

-viscosité faible à l'état fondu, permettant l'adhésion aux tissus dentaires, associée à une température de fusion la plus basse possible pour ne pas provoquer de nécrose pulpaire

-dureté équivalente à l'émail dentaire (Hv = 460 $daN.mm^{-2}$)

-insolubilité en milieu aqueux (pH = 7)

-biocompatibilité avec le milieu pulpaire

Les recherches bibliographiques nous ont révélé que l'hydroxyapatite de calcium, constituant minéral principal de la dent, de fusion élevée, (T_f = 1660°C), ne peut être coulée du fait de sa trop forte viscosité à l'état fondu . Il était donc indispensable de trouver un ou plusieurs composés qui, lui étant associés, joueraient le rôle de fondant . Notre choix s'est porté sur les verres à base de $NaPO_3$ et $Na_2B_4O_7$ dont les propriétés physico-chimiques étaient compatibles avec les critères précédemment énoncés . La présence d'apatite permet de renforcer de façon notable certaines propriétés (voir Chapitre II).

B-ESSAIS D'OBTURATION DE CARIES DENTAIRES ARTIFICIELLES

Préalablement, des essais de fusion par laser (tir de puissance 3W pendant 10s) ont été effectués sur les poudres de verres satisfaisant aux critères de choix. Ces essais avaient pour but d'écarter les compositions vitreuses qui, fondues, ne possédaient pas un mouillage suffisamment rapide.

Malgré ces essais préliminaires, il nous est vite apparu que l'adhésion sur la dentine des verres sélectionnés était difficile (carbonisation du tissu dentinaire au cours de la fonte empêchant toute adhésion)

Pour les essais d'obturation qui ont suivi, nous avons été contraints de trouver un composé servant de liant entre le tissu dentinaire et le verre d'obturation. Le monofluorophosphate de sodium possède un fort pouvoir mouillant, une faible température de fusion et peut être fondu sous l'action du faisceau laser grâce à sa forte absorption située vers 10 µm. L'application d'une fine couche de Na_2PO_3F sous forme de poudre, fondue sous l'impact laser, colle à la dentine sans formation importante de carbone . Le verre peut ensuite combler le reste de la cavité .

La couche du matériau à fondre était située à 5 cm environ de l'optique laser, la puissance était comprise entre 3 et 5 W et la durée de chaque coup de 10s.
Plusieurs remarques d'ordre général peuvent être formulées :

-dans les conditions opératoires définies ci-dessus, la quantité de poudre de verre tassée pouvant être fondue sous l'impact du faisceau laser ne pouvait excédée $1mm^2$ sur moins d'un mm d'épaisseur

-le nombre de tirs nécessaires au comblement augmente avec le volume de la cavité

-après application, le matériau de comblement apparaît vitrifié et fissuré par la forte trempe qu'il a subie.

Les nombreux essais effectués semblent montrer que l'association d'une couche adhésive à la dentine de Na_2PO_3F puis du verre borophosphate de comblement ($0{,}95NaPO_3$-$0{,}05Na_2B_4O_7$; $\lambda_{abs.}=11\mu m$; $Hv = 230\ daN.mm^{-2}$) pourrait être la solution la plus adaptée au comblement. Cependant , il reste deux difficultés à surmonter : obtenir une recristallisation partielle du matériau en surface, afin de lui donner une couleur blanchâtre proche de celle de l'émail, et éliminer les fissures liées à une trempe trop rapide du verre .

Des essais de balayage par un faisceau laser de faible puissance et défocalisé n'ont permis qu'une élimination partielle des fissures en surface , sans amener la recristallisation du verre. L'ajout de composés susceptibles d'entraîner la recristallisation n'ayant pas donné satisfaction, il était donc nécessaire de dissocier, matériau de comblement et matériau de surface . Le procédé devait donc se dérouler en trois étapes:

-1) dépôt de Na_2PO_3F

-2) comblement par le verre

-3) dépôt d'un matériau de surface.

Pour la dernière phase, l'utilisation de la vitrocéramique de composition 0,2 $Ca_5(PO_4)_3OH$-0,8 $NaPO_3$, proche de la limite du domaine vitreux contenu dans le système $NaPO_3$-$Na_2B_4O_7$-$Ca_5(PO_4)_3OH$ (voir Chapitre II), semble être un compromis acceptable entre l'esthétique de la surface (blanchâtre et lisse) et la facilité de dépôt de la couche (température de fusion modérée). Cette composition possède, en outre, une dureté équivalente à l'émail dentaire (Hv = 470 $daN.mm^{-2}$), une viscosité pas trop élevée à l'état fondue et une faible solubilité dans l'eau ($\sim 10^{-7}$ $g. cm^{-2}. mn^{-1}$ pour un pH = 7 à 100°C).

C-COMPORTEMENT THERMIQUE DE LA DENT AU COURS D'UN TRAITEMENT D'OBTURATION

L'échauffement lié à la fusion du matériau de comblement doit être compatible avec la survie de la pulpe dentaire [1-3]. A cet effet, nous avons suivi l'évolution de la température au niveau supérieur de la cavité pulpaire durant la durée de comblement d'une carie dentaire artificielle . Le procédé expérimental est schématisé à la Figure 1.

La courbe d'élévation de température dans la cavité pulpaire, en fonction du temps de remplissage est représentée à la Figure 2.

A partir de cette représentation nous constatons que :

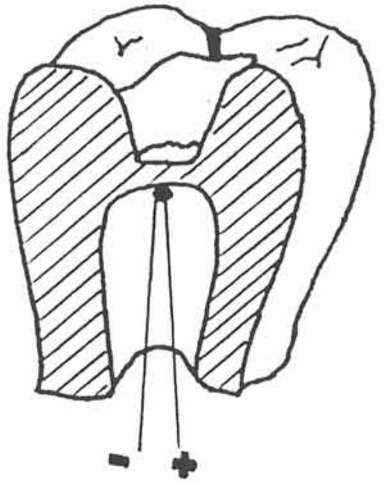

Figure 1: Schéma en coupe de la dent à obturer. Position du thermocouple au niveau de la pulpe dentaire

- le dépôt de Na_2PO_3F et le comblement par le verre nécessitent un nombre restreint de tirs laser
- le dépôt du matériau de surface (phase 3) est relativement long: il est nécessaire de procéder à de nombreux tirs laser pour avoir une bonne finition
- l'élévation de température globale au niveau de la cavité pulpaire n'excèdant pas 20°C ($\Delta T_{critique} = 25°C$) [4], celle-ci ne devrait pas, en première approximation, être suffisante pour provoquer soit nécrose de la pulpe, soit douleur chez le patient.

Notons qu'une cadence de tir rapide entraîne une diminution progressive du rendement du laser (échauffement) rendant plus difficile le comblement de la cavité dentaire et le dépôt de la couche de surface.

L'extraction des matériaux de comblement est difficile sans qu'il y ait destruction de la dent. L'observation à la loupe binoculaire montre une surface vitrocéramisée blanche avec pratiquement auncune fissure.

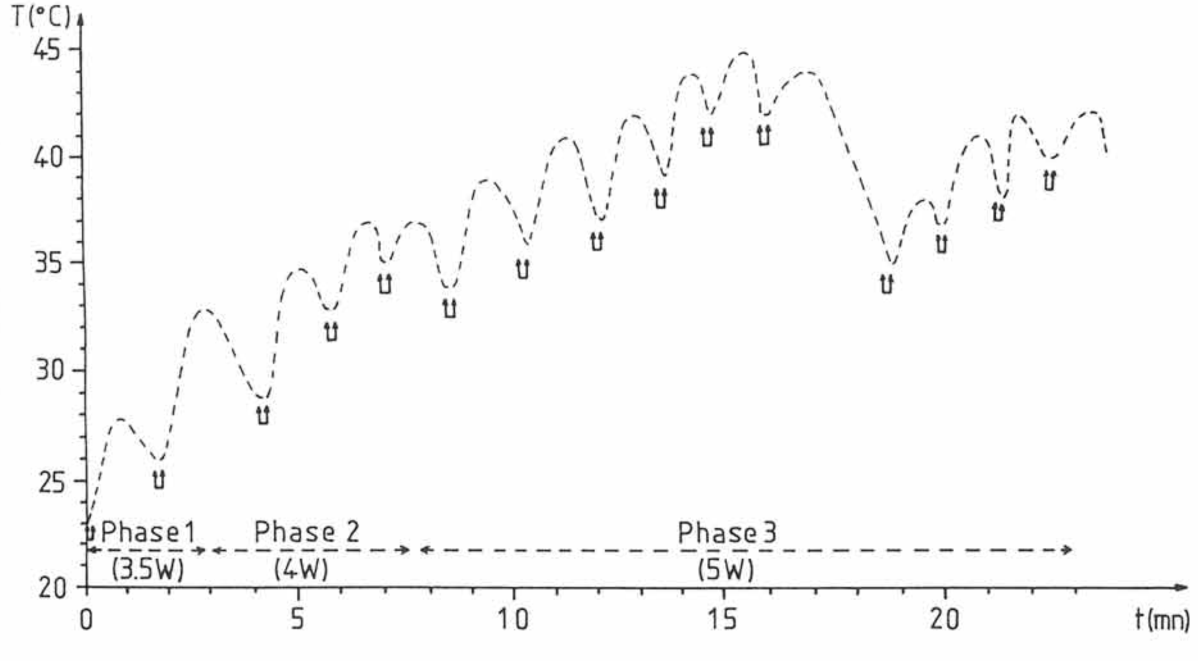

Figure 2 : Evolution thermique au niveau de la cavité pulpaire en fonction du temps d'obturation de la carie artificielle
Phase 1: Na_2PO_3F
Phase 2: verre de comblement: $0{,}95\ NaPO_3$-$0{,}05\ Na_2B_4O_7$
Phase 3: vitrocéramique de surface: $0{,}2\ Ca_5(PO_4)_3OH$-$0{,}8\ NaPO_3$
⇅: schématise un tir laser (10s)

D-CONCLUSIONS

Le but de ce travail était la recherche de nouveaux matériaux de restauration dentaire pouvant être fondus in situ par action d'un faisceau laser à gaz CO_2 .

De multiples essais nous ont conduit à réaliser l'obturation d'une carie artificielle par un processus en trois étapes :

1) dépôt d'une couche de Na_2PO_3F (adhésion à la dentine)

2) obturation à l'aide du verre de composition 0,95 $NaPO_3$-0,05 $Na_2B_4O_7$

3) dépôt d'une couche de surface de composition 0,2 $Ca_5(PO_4)_3OH$-0,8 $NaPO_3$ (aspect blanchâtre et très peu fissuré)

Cependant, si les deux premiers stades d'obturation semblent être assez satisfaisants, la couche de surface pourrait ne pas convenir pleinement: l'adhésion en bord de cavité et l'aspect de surface sont imparfaits.

En effet, le nombre de tirs laser nécessaire à la bonne finition de cette couche doit être limité pour ne pas conduire à un échauffement trop important de la pulpe dentaire. Ceci provient du fait qu'un matériau peut difficilement posséder à la fois une fusion modérée avec une faible viscosité à l'état liquide et être dur et insoluble en milieu aqueux. Ces difficultés peuvent être surmontées soit en acceptant une solution de compromis telle que le matériau de surface utilisé, soit en favorisant une propriété au détriment des autres. Avant d'envisager, si nécessaire, une nouvelle étape de recherche, il serait souhaitable d'effectuer des tests cliniques de biocompatibilité et de fiabilité sur des dents restaurées selon le procédé de comblement mis au point dans cette étude .

Références

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CONCLUSIONS GENERALES

Le but de ce travail était d'élaborer et d'étudier de nouveaux verres utilisables dans le domaine médical. Outre l'obligation d'être biocompatibles, ces matériaux, appelés alors biomatériaux, doivent posséder les propriétés physico-chimiques requises pour l'utilisation désirée.

Dans cette recherche de biomatériaux possédant d'une part, de bonnes résistances mécaniques et chimiques et d'autre part, des températures de transition vitreuse et de fusion modérées, notre choix s'est porté sur les verres obtenus par l'association de $NaPO_3$, $Na_2B_4O_7$ et d'hydroxyapatite de calcium ($Ca_5(PO_4)_3OH$) connue pour être le constituant minéral principal des tissus osseux. Ces verres ont été étudiés tant d'un point de vue physico-chimique que structural (RMN du ^{31}P MAS et du ^{11}B, absorption IR et diffusion Raman).

Afin de mieux comprendre l'influence de chaque composant sur les propriétés physico-chimiques et la structure des verres qu'ils forment, nous avons étudié, dans un premier temps (CHAPITRE I), les verres de composition $(1-x)\ NaPO_3 - x\ Na_2B_4O_7$ ($0 \leq x \leq 1$).

Les températures de transition vitreuse (Tg) et de cristallisation (Tc), la masse volumique (ρ), le volume molaire (V), la microdureté (Hv), la solubilité dans l'eau (S) et la longueur d'onde de coupure dans l'UV (λc) ont été mesurées en fontion de x. L'introduction de borate dans $NaPO_3$ provoque une augmentation rapide des paramètres tels que: Tg, Tc, ρ, et Hv et une diminution de S et λc. Pour x voisin de 0,2 (B/B+P=0,5), une discontinuité apparait dans l'évolution de Tg, V et Hv. Au delà, les valeurs de ces paramètres tendent de façon quasi régulière vers celles de $Na_2B_4O_7$.

Une corrélation a pu être effectuée entre l'évolution anormale de l'ensemble de ces propriétés et celles de la microstructure. Trois modèles structuraux représentatifs du domaine vitreux ont été proposés:

i)-$0 \leq x \leq 0{,}05$ ($0 \leq B/B+P \leq 0{,}17$)

L'ajout de $Na_2B_4O_7$ dans $NaPO_3$ vitreux, constitué de chaînes dont la longueur moyenne est de 20 tétraèdres $O_{2/2}PO_2^-$, provoque un raccourcissement de celles-ci. En effet, les atomes de bore principalement tétracoordinés viennent connecter les chaînons de plus en plus courts, au fur et à mesure que la quantité d'atomes de bore augmente. L'excès de charge d'un tétraèdre $BO_{4/2}^-$ est compensé par celle positive d'un tétraèdre $(O_{2/2}PO_2^{2-}, 2Na^+)^+$ et non par celle d'un ion sodium (unité C_{Na}) comme dans $Na_2B_4O_7$. Ce mode de compensation de charge s'accompagne donc de la formation de groupements C_P de type $(O_{3/2}\ BOPO_{5/2})^{2-}$. Ce processus conduit à la création d'une structure ramifiée, tridimensionnelle, responsable de l'amélioration des propriétés physico-chimiques telles que Hv et S^{-1}. Cette ramification aléatoire conduit à un tel désordre que la température de cristallisation n'est plus observable, signe d'une très grande stabilité vitreuse.

ii)-$0,05 < x \leq 0,20$ ($0,17 < B/B+P \leq 0,50$)

Le raccourcissement de la longueur moyenne des chaînes entre bore se poursuit, jusqu'à la formation d'unités $(O_{2/2}PO_2^-, Na^+)$, $(O_{2/2}PO_2^{2-}, 2Na^+)^+$ et $(O_{3/2}PO^-, Na^+)^+$ "isolées". Afin de conserver une bonne adéquation entre les informations structurales et la composition chimique de ces verres, de nouveaux groupements borophosphatés de type C_P $(O_{3/2}BOPO_{4/2})^-$ doivent exister dans la structure vitreuse. De plus, en raison de la diminution du rapport $B_{IV}/B_{IV}+B_{III}$, atteignant 0,75 pour x=0,2, un certain nombre de groupements $(O_{2/2}BOPO_{5/2})^-$ apparaissent progressivement dans le verre.

iii)-$0,20 < x \leq 1.00$ ($0,50 < B/B+P \leq 1.00$)

Dans ce domaine de composition, les cycles boratés constitués d'atomes de bore tri- et tétracoordinés en quantité quasi équivalente, comme dans $Na_2B_4O_7$, prédominent dans le verre. Le passage de la structure de type "plus phosphate" à celle de type "plus borate" peut être corrélé à la présence de la discontinuité dans l'évolution de Tg et Hv. Les unités phosphatées "isolées", de moins en moins nombreuses lorsque x augmente, s'insèrent aléatoirement entre les cycles boratés, provoquant d'une part, un important désordre se traduisant par l'absence de Tc, mais également un affaiblissement du réseau vitreux (augmentation de λc et S). Enfin, pour les plus faibles concentrations en phosphate (x≥0,9), quelques unités terminales $O_{1/2}PO_3^{2-}$ ainsi que des monomères apparaissent dans la structure.

Notons que l'ensemble de ces hypothèses structurales a pu être confirmé par une étude par XPS (P_{2s}, $P_{2p(3/2-1/2)}$, B_{1s}, Na_{1s} et O_{1s}) faite en collaboration avec le Laboratoire de Physico-Chimie Moléculaire de Pau, non présentée dans ce mémoire.

L'étude des propriétés physico-chimiques et structurales des verres de composition (1-X) $[NaPO_3\text{-}RNa_2B_4O_7]$ - X $Ca_5(PO_4)_3$ OH avec $0 < X \leq 0{,}12$ a constitué la deuxième partie de ce travail (CHAPITRE II).

La présence d'hydroxyapatite, provoque une forte augmentation de l'ensemble des caractéristiques physico-chimiques étudiées (Tg, Tc, ρ, V, Hv et S^{-1}) sans modification de l'évolution anormale observée pour les verres du pseudo-binaire (v.s. R avec X=0).

L'addition de $Ca_5(PO_4)_3$ OH , constitué de tétraèdres PO_4^{3-} isolés, conduit pour les verres phosphatés (R=0) à une dépolymérisation du réseau formateur. Ceci se traduit par un raccourcissement de la longueur moyenne des chaînes métaphosphatées, entraînant l'apparition de nombreuses unités terminales. Celles-ci pouvent être "connectées" par l'intermédiaire des ions Ca^{2+} en formant les groupements:

$\{(O_{1/2}PO_3^-, Na^+)^- Ca^{2+} {}^-(Na^+, {}^-O_3PO_{1/2})\}$ et $\{(O_{1/2}PO_3)^{2-} 2Ca^{2+} {}^{2-}(O_3PO_{1/2})\}$.

Notons qu'en limite de zone vitreuse le réseau vitreux est essentiellement constitué d'une association de chaînons triphosphates.

Dans les verres borophosphatés sodocalciques contenant peu de borate (0<R<0.25), les unités $BO_{4/2}^-$, en nombre légèrement plus faible que dans les verres borophosphatés de sodium, contribuent, comme dans ces derniers, à une ramification désordonnée des chaînons phosphatés préservant ainsi un domaine vitreux relativement large. L'édifice structural reste sensiblement le même que celui des verres issus du pseudo-binaire. Cependant, il est constitué de chaînons phosphatés plus courts ce qui se traduit par une diminution de la compacité (V^{-1}). De plus, comme dans les verres phosphatés sodocalciques (R=0), les ions Ca^{2+} renforcent la cohésion interchaînons. L'augmentation de la résistance à l'eau et de la dureté peut être attribuée à cet effet.

La présence d'un domaine vitreux étroit le long du pseudo-système $NaPO_3$ - $Na_2B_4O_7$, dans le domaine de composition R>0,5, ne permet pas de déceler des modifications structurales importantes par rapport aux verres borophosphatés de sodium. En effet, le pouvoir destructeur de l'hydroxyapatite sur le réseau vitreux borophosphaté est prépondérant sur l'effet ramificateur des unités $BO_{4/2}^{-}$, maintenant engagées majoritairement dans les cycles boratés.

La dernière partie de ce travail (CHAPITRE III) a été consacrée à la mise au point d'un procédé d'obturation de carie dentaire par un matériau adapté, fondu in situ, sous l'action d'un faisceau laser CO_2. Outre le fait que le matériau choisi devait être biocompatible, il devait aussi posséder les propriétés requises permettant, d'une part, de faciliter l'opération de comblement et l'adhésion aux tissus dentaires (absorption importante à λ=10,6µm, viscosité faible avec une grande mouillabilité à l'état fondu) sans entraîner de nécrose pulpaire (Tg et Tf modérées) et d'autre part, de présenter les caractéristiques esthétiques (blancheur, brillance), physiques (dureté) et chimiques (insolubilité) de l'émail dentaire.

Des essais préliminaires ont montré qu'il n'était pas possible d'obtenir une bonne restauration de la dent en utilisant qu'un seul matériau. Le procédé le mieux adapté à l'obturation de caries artificielles nécessitant l'emploi de trois matériaux s'établit comme suit:

i)-fusion d'une mince couche de Na_2PO_3F sur les parois de la cavité dentaire afin de pallier la carbonisation des tissus dentinaires et favoriser l'adhésion du matériau de comblement

ii)-obturation de la cavité par le verre de composition 0,95 $NaPO_3$ - 0,05 $Na_2B_4O_7$

iii)-fusion en surface d'une vitrocéramique de composition 0,8 $NaPO_3$ - 0,2 $Ca_5(PO_4)_3OH$ (λ_{abs}=11µm, Hv=470 daN.mm^{-2} et S=10^{-7} g. cm^{-2}. mn^{-1} pour un pH = 7 à 100°C)

L'opération de comblement nécessite environ 25 mn et n'entraînerait pas, à priori, de nécrose pulpaire.

L'aspect général d'une dent restaurée par ce procédé montre quelques imperfections, notamment au niveau de l'état de surface et de l'adhésion à l'émail dentaire. Seuls, les résultats de tests cliniques permettront de nous prononcer sur la fiabilité de ce procédé. Dans le cas d'une réponse favorable, ce procédé ne peut être optimisé puis développé que si des améliorations sensibles sont apportées au laser CO_2 miniaturisé servant à la fusion, in situ, des matériaux de comblement (refroidissement de la cavité, maniabilité, etc...).

Outre l'application de ces verres comme biomatériaux, il est intéressant de souligner que certaines compositions, étudiées dans ce mémoire, présentent des propriétés spécifiques les rendant très attractives dans le domaine des matériaux pour l'opto-électronique.