



RAMAN SPECTRUM STUDIES OF THE COORDINATIONS OF ALUMINIUM AND BORON IN Na₂O-Al₂O₃-B₂O₃-P₂O₅ GLASSES

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RAMAN SPECTRUM STUDIES OF THE COORDINATIONS OF ALUMINIUM
AND BORON IN $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ GLASSES

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Résumé—Les états de coordination d'aluminium et de bore dans le verre $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ ont été étudiés par la technique de spectroscopie Raman. L'étude montre que quand les ions de bore et d'aluminium existent simultanément dans le verre phosphate, il est possible que les ions de bore forment les tétraèdres BO_4 avant les ions d'aluminium. Et les nombres de coordination de ces premiers sont trois et quatre et ceux de Al quatre et six.

Abstract - The coordination states of aluminium and boron in $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses have been studied by means of Raman spectroscopy. The study shows that when boron and aluminium ions exist simultaneously in phosphate glasses, it is possible that boron ions form BO_4 tetrahedra prior to aluminium ions, and the former has three and four coordinations while the latter has four and six.

I - INTRODUCTION

We have shown the Raman spectra of sodium aluminophosphate glasses in reference /1/. The reason for such interest is the fact that lectures about Raman spectrum studies of the structure of glasses in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ system were rarely reported and that certain glasses in this system are good sodium ion conductors. In order to further improve the ion conductivity of the glasses, boric oxide was added to the ternary glasses.

As is well known, the role of aluminium ions in the glass structure is rather different from that of boron ions. Al^{+3} ions which exist in 4 and 6 coordinations can act as glass forming and modifying cation respectively, while both 3 and 4 coordination B^{3+} ions are part of the glass network. There is no doubt that this makes the structure of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses much more complex than that of $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses. As a result, the effect on the glass conductivity is also different. The article is aimed at dealing with the glass structure through investigating the changes of boron and aluminium coordinations by means of Raman spectroscopy.

II - EXPERIMENTAL

The designed compositions of the glasses are shown in the Figs. 1-3. Parallel polarized (XX) Raman spectra of glasses were measured on a Spex Ramalog spectrometer at a scattering angle of 90° . The excitation source was the 5145\AA line of Ar ion laser. The laser power was 500mw.

III - DISCUSSION OF RESULTS

Table 1, where the Raman peaks of different kinds of groups which may appear in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses, is used as a reference for discussing the changes of Raman spectra due to B_2O_3 added to the glasses.

Table 1. Raman peaks of different kinds of groups which may appear in the $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses

group	peaks cm^{-1}	$\text{Na}_2\text{O}/\text{P}_2\text{O}_5$
$(\text{PO}_3)_n^{n-}$	1280, 1170, 700, 645 /2,3/	1
$(\text{P}_4\text{O}_{13})^{6-}$	1120, 540 /3/	1.5
$(\text{P}_3\text{O}_{10})^{5-}$	1112, 540 /3/	1.67
$(\text{P}_2\text{O}_7)^{4-}$	1060-1080, 720 /4/	2
AlO_4	760 /5/	/
AlPO_4	1040, 600, 470, 300 /1/	1

1. Fig. 1 shows the Raman spectra of $45\text{Na}_2\text{O} \cdot x\text{B}_2\text{O}_3 \cdot (5-x)\text{Al}_2\text{O}_3 \cdot 50\text{P}_2\text{O}_5$ and $40\text{Na}_2\text{O} \cdot x\text{B}_2\text{O}_3 \cdot (10-x)\text{Al}_2\text{O}_3 \cdot 50\text{P}_2\text{O}_5$ acidic glasses. Compared with table 1, it becomes clear that the peaks which appear in both figs. 1a and d can be attributed to the vibration of glass network which consists of major numbers of $(\text{PO}_3)_n^{n-}$ chains and rings, a small number of $(\text{P}_4\text{O}_{13})^{6-}$ and $(\text{P}_3\text{O}_{10})^{5-}$ groups. When Al_2O_3 is replaced by B_2O_3 up to 10 mol%, the Raman spectra (cf. figs. 1b-c, e-h) show no great changes, except the gradual disappearance of the peak at 540 cm^{-1} caused by $(\text{P}_4\text{O}_{13})^{6-}$ and $(\text{P}_3\text{O}_{10})^{5-}$ groups. Disappearance of the polyphosphate groups resulting from the replacement of Al_2O_3 by B_2O_3 may be interpreted that there is a difference between coordination states of aluminium in phosphate and borate glasses. When adding Al_2O_3 to borate glasses with low alkali-to-boron ratios, boroxol groups form again because of the replacement of BO_4 tetrahedra in borate rings by AlO_4 tetrahedra /6,7/. In other words, the Al^{3+} ions form AlO_4 units prior to B^{+3} ions in borate glasses. However, it has been proved that in acidic $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{P}_2\text{O}_5$ glasses with $\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5 < 0.63$, nearly all of Al^{+3} ions are six coordinated. The role of Al^{+3} ions in the glass structure is the same as that of Na^+ ions /1/. As soon as B_2O_3 is added to these glasses, we think it is possible that some of them may scavenge the necessary oxygen ions from Na_2O and Al_2O_3 connected with tri- and tetraphosphate groups, forcing polymerization of the phosphate network and themselves changing from 3 into 4 coordination. Therefore, the disappearance of the peak at 540 cm^{-1} due to polyphosphate groups with higher ratio of $\text{Na}_2\text{O}+\text{Al}_2\text{O}_3/\text{P}_2\text{O}_5$ is reasonable. In the Raman spectra studied, no

peaks due to borate rings with BO_4 units (720 , 750 and $780 \text{ cm}^{-1}/7/$) are observed. This might mean that at low concentration of boron ions, it is present as "loose" BO_4 tetrahedra in the phosphate network.

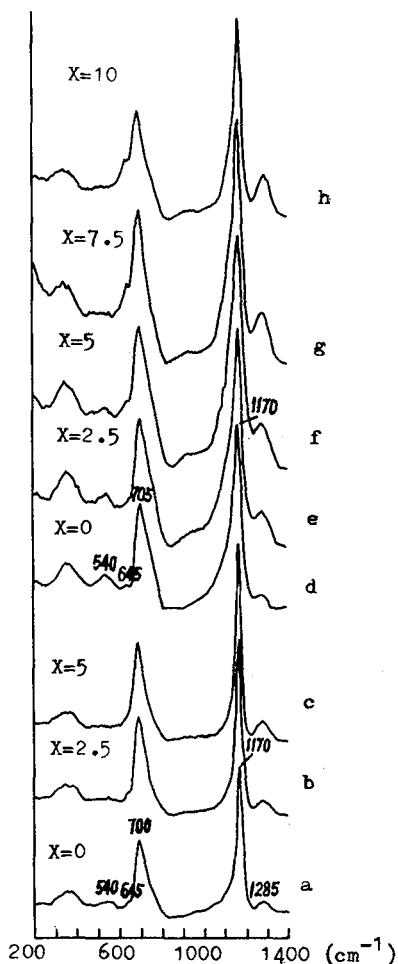


Fig. 1. Raman spectra of $45\text{Na}_2\text{O} \cdot x\text{B}_2\text{O}_3 \cdot (5-x)\text{Al}_2\text{O}_3 \cdot 50\text{P}_2\text{O}_5$ (a-c) and $40\text{Na}_2\text{O} \cdot x\text{B}_2\text{O}_3 \cdot (10-x)\text{Al}_2\text{O}_3 \cdot 50\text{P}_2\text{O}_5$ glasses (d-h).

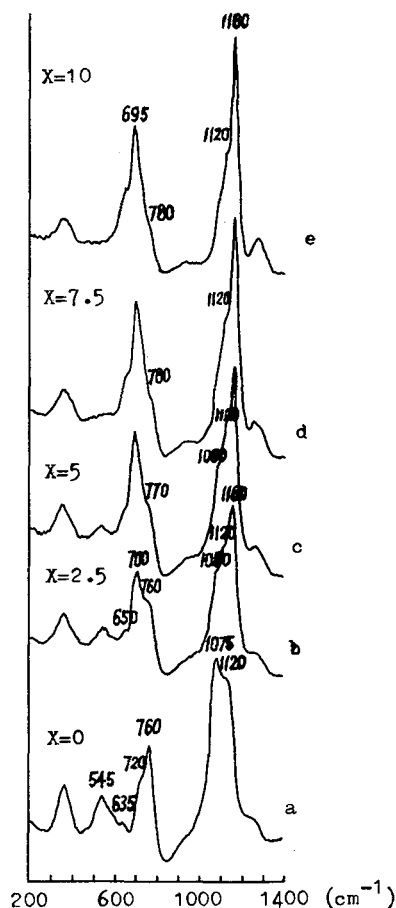


Fig. 2. Raman spectra of $45\text{Na}_2\text{O} \cdot x\text{B}_2\text{O}_3 \cdot (10-x)\text{Al}_2\text{O}_3 \cdot 45\text{P}_2\text{O}_5$ glasses.

2. Fig.2 shows the Raman spectra of $45\text{Na}_2\text{O} \cdot x\text{B}_2\text{O}_3 \cdot (10-x)\text{Al}_2\text{O}_3 \cdot 45\text{P}_2\text{O}_5$ neutral glasses. Fig.2a is due to AlO_4 tetrahedra, $(\text{P}_2\text{O}_7)^{4-}$, $(\text{P}_3\text{O}_{10})^{5-}$ and $(\text{P}_4\text{O}_{13})^{6-}$ groups (cf. table 1). It can be observed that replacement of 2.5 mol% Al_2O_3 by B_2O_3 leads to a decrease in the intensity of the peaks of various phosphate groups shown in fig.2a and a reformation of the peaks at 1160 and 700 cm^{-1} assigned to stretching vibrations of PO_2 and p-o-p in $(\text{PO}_3)_n^{n-}$ groups. When Al_2O_3 is replaced up to 7.5 mol% by

B_2O_3 , the peak at 1080 cm^{-1} due to $(P_2O_7)^{4-}$ groups vanishes, and peaks at 1120 and 540 cm^{-1} due to $(P_3O_{10})^{5-}$ and $(P_4O_{13})^{6-}$ groups tend to vanish too. At the same time, the peak at 760 cm^{-1} caused by AlO_4 tetrahedra first degenerates into shoulder, then the shoulder is replaced by the peak at $770\text{--}780\text{ cm}^{-1}$ attributed to tetraborate groups with BO_4 units [7], and it seems to display a structural characteristic similar to the $45Na_2O \cdot 10B_2O_3 \cdot 45P_2O_5$ glass (cf. fig.2e). The regular change in spectra again show that, with substituting B_2O_3 for Al_2O_3 , Al^{+3} ions change from 4 into 6 coordination and phosphate network polymerizes. The ultimate result of these changes must have offered $O^{=}$ ions, boron ions needed for changing from 3 into 4 coordination.

3. Fig. 3 shows the Raman spectra of $45Na_2O \cdot xB_2O_3 \cdot (20-x)Al_2O_3 \cdot 35P_2O_5$ alkaline glasses. As compared with table 1, it is obvious that fig.3a can be attributed to

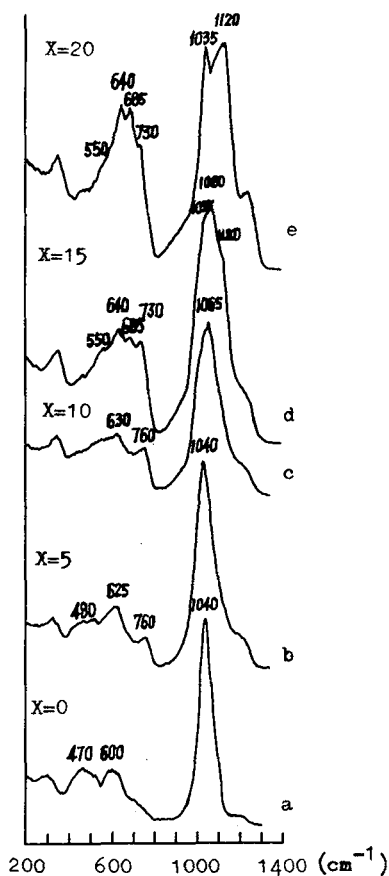
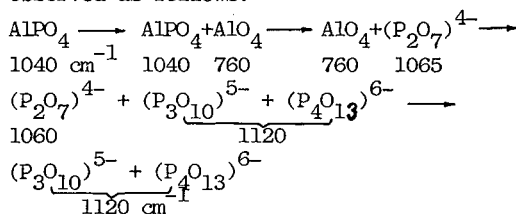


Fig. 3. Raman spectra of $45Na_2O \cdot xB_2O_3 \cdot (20-x)Al_2O_3 \cdot 35P_2O_5$ glasses

the vibration of $AlPO_4$ groups. Substituting B_2O_3 for Al_2O_3 up to 20 mol%, the development of aluminophosphate network can be observed as follows:



From what is mentioned above, it can be deduced that substituting B_2O_3 for Al_2O_3 first leads to the depolymerization of $AlPO_4$ network, and then urges the polymerization of phosphate network. The latter process is very similar to those in acidic and neutral glasses. However, the role of boron in phosphate glasses with higher B_2O_3 seems to be unique. For $45Na_2O \cdot 20B_2O_3 \cdot 35P_2O_5$ glass, besides strong peak at 1120 cm^{-1} due to tri- and tetraphosphate groups, its Raman spectrum also shows the peaks at 1035 , 730 , 685 and 640 cm^{-1} (cf. fig.3e). The peaks at 730 685 and 640 cm^{-1} can be associated with the vibrations of diborate groups with two BO_4 units and ring-type metaborate groups with one NBO on each BO_3 unit [7]. But the peak at 1035 cm^{-1} cannot be so readily assigned to the vibration of a specific structural

unit. Although this peak also appears in the Raman spectrum of $\text{Al}_2\text{O}_3=5\text{ mol\%}$ glass (cf. fig.3d), it can not be linked with the vibration of AlPO_4 groups, because Al_2O_3 is absent in the 20 mol% B_2O_3 glass. On the other hand, T. Tsuchiya et al /8/ pointed out that the Raman peaks of the crystalline BPO_4 were found at 485 and 1130 cm^{-1} , and the ratio between their scattering intensity was about 4. The peak at 485 cm^{-1} was not found in figs.3d-e, so we have no reason to associate 1035 cm^{-1} peak with the vibration of BPO_4 groups in which the excess of negative charge on the BO_4 units is compensated by the excess of positive charge on the PO_4 units. In other words, the P=O double bond is open in this case. In order to distinguish it from $(\text{BPO}_4)^-$ groups in which the excess of negative charge on the BO_4 units is compensated by the Na^+ ions, the above-mentioned BPO_4 groups are written as $(\text{BPO}_4)^0$. Our tentative conclusion is that the 1035 cm^{-1} peak is due to $(\text{BPO}_4)^-$ groups.

IV - CONCLUSIONS

In $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-B}_2\text{O}_3\text{-P}_2\text{O}_5$ glasses, both aluminium and boron ions have two types of coordination, the former has 4 and 6 while the latter has 3 and 4. With the increase in the ratio of $\text{B}_2\text{O}_3/\text{Al}_2\text{O}_3$, aluminium and boron ions change from 4 into 6 and from 3 into 4 respectively. It means that when B^{+3} and Al^{+3} ions exist simultaneously in phosphate glasses, B^+ ions form BO_4 tetrahedra prior to Al^{+3} ions. In glasses containing higher B_2O_3 , some of B^{+3} ions exist in the form of borate groups with non-bridging oxygens.

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