Network Structure of Borophosphate Glasses (Part 2)

Raman Spectra of Potassium Borophosphate Glasses

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ホウリン酸塩ガラスの網目構造 (第2報)

カリウムホウリン酸塩ガラスのラマンスペクトル

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Raman spectra have been measured for potassium borophosphate glasses of compositions $(1-x)[K_2O \cdot 2B_2O_3] - x[K_2O \cdot 2P_2O_5]$ ($0.1 < x < 0.9$). The observed bands are assigned to six-membered borate rings, phosphate chain or network composed of $O=PO_{3/2}$ and KPO_3 units by reference to the spectra of related crystals. Bands at 1030, 720, 600 and 550 cm^{-1} have been attributed to borophosphate networks, and the 720 cm^{-1} band is tentatively assigned to six-membered borophosphate clusters incorporating $[PO_{4/2}]^+$ or $O=PO_{3/2}$ units. Bands due to BPO_4 type network ($1130, 1080, 485\text{ cm}^{-1}$) as well as those due to a metaborate ring or chain have not been found. Coexistence of $BO_{3/2}$ and $O=PO_{3/2}$ units is proposed.

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1. Introduction

Yun and Bray¹⁾ have measured ^{11}B NMR spectra for the glasses in the system $K_2O\text{-}B_2O_3\text{-}P_2O_5$ to derive the fraction of four-coordinated boron atoms, N_4 , and proposed the absence of 'asymmetric' borate unit BO_3^- having a non-bridging oxygen. They stated " K_2O is proportionally shared between borate and borophosphate (BPO_4) networks for the ratio $P_2O_5/B_2O_3 < 1$, and between borophosphate (BPO_4) and phosphate networks for $P_2O_5/B_2O_3 > 1$." The present authors, however, pointed out in the previous paper²⁾ that K_2O is distributed to B_2O_3 and P_2O_5 in proportion to their mixing ratio, and that the variation of N_4 can be reproduced by assuming either of the two mechanisms: (1) presence of BO_3^- units or (2) coexistence of $PO_{2.5}$ ($O=PO_{3/2}$) and $BO_{3/2}$ units. Therefore, $KBO_{4/2}$, $KOBO_{2/2}$ and $BO_{3/2}$ will be formed from the reaction $K_2O + B_2O_3$, while KPO_3 and $PO_{2.5}$ from $K_2O + P_2O_5$. A reaction between $BO_{3/2}$ and $PO_{2.5}$ units gives four-branching tetrahedral units, $[PO_{4/2}]^+$ and $[BO_{4/2}]^-$,

but, according to the second mechanism, the reaction would not exhaust the $PO_{2.5}$ or $BO_{3/2}$ units and some of them remain in glass without changing to the $[PO_{4/2}]^+$ or $[BO_{4/2}]^-$ units. In addition to this uncertainty in the constituent units,

an attention should be paid to the formation of some borophosphate clusters. Such cluster formation has been rarely referred to in the literature despite that alkali or alkaline earth borate networks are usually interpreted as consisting of several borate groups such as boroxol, tetraborate, triborate and diborate groups.^{3),4)} Since both borate and phosphate units involve π -bonding and easily construct ring type networks, it is highly possible for them to get together and compose some ring type clusters. Ray measured Raman spectra⁵⁾ of the potassium borophosphate glasses to evaluate N_4 or cross-link density but did not touch upon such cluster formation.

In the present experiment, Raman spectra have been measured for the glasses in the pseudo-binary system $K_2O \cdot 2(1-x)B_2O_3 \cdot 2xP_2O_5$ where x ranges from 0.1 to 0.9. The interest of the study rests on clarifying the structural change and interpreting the constitution of the glasses on the basis of tentative assignment of Raman spectra.

2. Experimental procedure

Potassium borophosphate glasses were prepared by melting mixtures of potassium carbonate, boron oxide and phosphorus pentoxide in an alumina crucible with a cover, varying x from 0.1 to 0.9.²⁾ The analyzed composition did not deviate so much from the batch composition except for

water and aluminum oxide contamination, as indicated previously.²⁾ Therefore, parameter x in the batch composition was used to represent the glass. Raman spectra were measured by a laser-Raman spectrometer (Nippon Bunko JASCO NR-1000) with Ar-laser beam (514.5nm). Crystalline BPO_4 (high cristobalite type, JCPDS 14-696) was prepared⁶⁾ and its spectrum was also recorded.

3. Results and discussion

3.1 Raman spectra of the borophosphates

Raman spectra of the borophosphate glasses are illustrated in Fig. 1 where the figures indicate the Raman shift frequencies in cm^{-1} . Figure 2 indicates the variation in peak positions of these Raman bands as a function of x , which are numbered as band (a) through (j) from top to bottom. Raman spectrum for crystalline BPO_4 is also indicated in Fig. 1 as the reference because the formation of an $\text{O}_3\text{B}-\text{O}-\text{PO}_3$ (BPO_4) unit has

Fig. 1. Raman spectra of the potassium borophosphate glasses of composition $\text{K}_2\text{O} \cdot 2(1-x)\text{B}_2\text{O}_3 \cdot 2x\text{P}_2\text{O}_5$. The spectrum for cristobalite type BPO_4 crystal is also shown. The figures represent the Raman shift.

Fig. 2. Variation of the peak position of Raman bands for glasses of composition $\text{K}_2\text{O} \cdot 2(1-x)\text{B}_2\text{O}_3 \cdot 2x\text{P}_2\text{O}_5$, plotted as a function of x .

been proposed in those glasses.^{1,2)} The crystal has three major bands at 240, 485 and 1130 cm^{-1} as well as some other weaker bands. The 450 cm^{-1} band for the glasses might have the same origin as that of the strongest band at 485 cm^{-1} of the crystal. However, this assignment is not probable because the glasses have no band corresponding to 240 cm^{-1} band of BPO_4 crystal and the intensity of the 450 cm^{-1} band for the glasses is reduced with increase in x , despite that the amount of the BPO_4 unit should increase with x up to $1/2$. It follows that the 485 cm^{-1} band is due to a lattice vibration of BPO_4 crystal, and a borophosphate network like that of cristobalite type BPO_4 crystal is absent in the glasses.

3.2 Raman shifts characteristic of some structure groups

The structure groups constructing borate networks show characteristic Raman bands which are applicable to confirm the presence of such groups in glass. Therefore, it is convenient here to

Table 1. Raman bands characteristic of borate and phosphate groups and units.

group/unit	Raman shift/ cm^{-1}	crystal*
orthoborate	905	$3\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$
pyroborate	840	$2\text{Na}_2\text{O} \cdot \text{B}_2\text{O}_3$
metaborate ring	610	$\text{K}_2\text{O} \cdot \text{B}_2\text{O}_3$
chain	720	$\text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$
triborate	765	$\text{K}_2\text{O} \cdot 3\text{B}_2\text{O}_3$
diborate	730	$\text{Li}_2\text{O} \cdot 2\text{B}_2\text{O}_3$
PO_2 (asym)	1272	
(sym)	1167	NaPO_3
P-O-P	685	Graham's salt
P-O	338	

* Borates: ref. 7, NaPO_3 : ref. 8.

summarize the Raman shift for the borate groups whose presence is expected in the glasses. Table 1 represents the peak position of the strongest band after Konijnendijk⁷⁾ for each crystal consisting only of the indicated group. Glassy NaPO₃ (Graham's salt) has four stronger Raman bands⁸⁾ which are also cited in the table as the reference bands originated from the phosphate chain.

3.3 Assignment of the Raman bands and constitution of the borophosphate glasses

3.3.1 Raman bands for borate and phosphate network or chain

Four bands found in the glass with $x=0.9$ are assignable to the phosphate network: 1315 and 1170 cm⁻¹ bands, (a and b in Fig. 2), to asymmetric and symmetric PO₂ vibration, and 690 cm⁻¹ band (f) to P-O-P one as in the sodium metaphosphate.⁸⁾ A weaker band (j) at 320 cm⁻¹ is due to a P-O bending mode, which can be seen in all of the present glasses. With decrease in x from 0.9 to 0.1, the intensity of the PO₂ bands decreases, and their positions shift to lower frequency until they reach 1190 and 1090 cm⁻¹ at $x=0.1$. Thus, the band at 980/1010(shoulder) cm⁻¹ for $x=0.1$ originates from a structure other than the simple phosphate network.

The borophosphate glass with $x=0.1$ shows two bands (d and i) at 770 and 450 cm⁻¹ which are also found for 3K₂O·7B₂O₃ glass.⁷⁾ The former band is due to a breathing vibration of six-membered borate ring with one or two BO₄ units.³⁾ The decrease of this band in intensity indicates the decrease in the amount of such borate rings. One may consider that such decrease in the borate rings should be associated only with the decrease in the total amount of B atoms in the glasses. This interpretation does not fully account for the structure variation because several bands are found which cannot be assigned either to borate groups or to phosphate network, e. g. the bands at 720 and 980 cm⁻¹ for $x=0.1$. As they grow with x but disappear above $x=0.7$, they should be ascribed to some borophosphate bonds or clusters. However, since the presence of asymmetric BO₃⁻ units has also been proposed,²⁾ it might be convenient to examine the presence of B-O⁻ non-bridging bonds in glass before discussing the formation of borophosphate clusters.

3.3.2 Absence of Raman bands for BO₃⁻ units

The B-O non-bridging bonds are found in the ortho-, pyro- and metaborate groups. The Raman spectra in Fig. 1 have no bands corresponding to the ortho- and pyro-borate groups which may be found near 905 and 840 cm⁻¹. Potassium metaborate ring gives a band near 610 cm⁻¹ as indicated

in Table 1, and a band might be found around 720 cm⁻¹ if the metaborate chain were formed in the present borophosphate glasses. From the lower probability of presence of the asymmetric BO₃ units, less than 20%,²⁾ and the intensity of the bands (e and g) at 720 and 600 cm⁻¹ is as high as that of 770cm⁻¹ band, it is not plausible to assign these two to such borate groups in which the asymmetric units are incorporated. The gradual blue shift from 1190 to 1315 cm⁻¹ of the asymmetric PO₂ vibration band (a) suggests that the PO_{2.5} units are mixed up with metaphosphate units KPO₃ (middle groups) to form the phosphate network. On these basis, it is concluded that the asymmetric BO₃ units are not formed in the borophosphate system and that the BO₃ and PO_{2.5} units coexist in the glasses.

3.3.3 Formation of borophosphate clusters and constitution of glass

On the basis of discussion in 3.3.2), one can assign, though speculatively, the bands near 1030, 720, 600, and 550 cm⁻¹ (c, e, g, and h) to the borophosphate clusters or bonds. Judging from the similarity in band position to the borate ring, the 720 cm⁻¹ band (e) can be attributed to a breathing vibration of a six-membered borophosphate ring with a four-branching [PO₄]⁺ unit. Its formal positive charge will be compensated by a [BO_{4/2}]⁺ unit outside or incorporated in the borophosphate ring cluster. It is also possible for the PO_{2.5} unit to be involved in the ring. The intensity of the 1030 cm⁻¹ band (c) varies in the same way as that of the 720cm⁻¹ band. Therefore, one may also assign band c) to the PO₂ vibration of the PO₄ units ([PO₄]⁺ or O=PO_{3/2}) involved in the borophosphate ring. Since P-O bridging bonds are longer than B-O bonds, the rings are not planar. Such clusters corresponding to bands (d) and (e) decrease and disappear near $x=0.7$ because of decrease in BO_{3/2} units to form the clusters. In turn, a network similar to that of diphosphate is formed in glass.

This tentative assignment of the Raman bands to the borophosphate network indicates that the PO₂ and borate ring vibration experiences a red shift when B and P atoms are mixed up to form a borophosphate network. It is likely, then, that the band (f) at 690 and 685 cm⁻¹ due to P-O-P for $x=0.9$ and 0.7, respectively, takes the red shift when one of the P atoms is replaced by B. Therefore, the bands (g) and (h) near 600 and 550 cm⁻¹ can be attributed to P-O-B bonds, but it is still uncertain in which network the P-O-B bonds are incorporated, rings or chains, or which cross-linking state the two atoms take, three-branching or four-branching.

4. Summary

Raman spectra have been measured for the potassium borophosphate glasses. The observed bands are assigned to six-membered borate rings, phosphate chain or network composed by $\text{O}=\text{PO}_{3/2}$ or KPO_3 units and six-membered borophosphate clusters incorporating $[\text{PO}_{4/2}]^+$ or $\text{O}=\text{PO}_{3/2}$ units by taking the Raman bands characteristic of the borate and phosphate units in the literature as the reference. Crystalline BPO_4 type network is absent in the present glasses. The following four bands have been attributed to the borophosphate units; 1030 cm^{-1} to PO_2 with the P atom bonded to B, 720 cm^{-1} to the breathing vibration of six-membered B-O-P rings, 600 and 550 cm^{-1} to P-O-B bonds. The coexistence of the BO_3 and $\text{PO}_{2.5}$ have also been proposed.

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References

- 1) Y. H. Yun and P. J. Bray, *J. Non-Cryst. Solids*, **30**, 45-60(1978).
- 2) A. Osaka, M. Ikeda, H. Ohbayashi and K. Takahashi, *Seramikkusu Ronbunshi*, **96**, 236-39 (1988).
- 3) D. L. Griscom in "Borate Glasses" (Materials Science Research, Vol. 12), Ed. L. D. Pye, V. D. Frechette and N. J. Kreidl, Plenum Press, New York (1978) pp.11-149.
- 4) A. Osaka and K. Takahashi, *Yogyo-Kyokai-Shi*, **91**, 374-77(1983).
- 5) N. H. Ray, *Phys. Chem. Glasses*, **16**, 75-80(1975).
- 6) A. Osaka, K. Takahashi and M. Ikeda, *J. Mater. Sci. Lett.*, **3**, 36-38(1984).
- 7) W. L. Konijnendijk, Philips Res. Reports, Suppl. 1975, No.1, Eindhoven, Netherlands.
- 8) A. Bertoluzza, A. M. Marinangeli, P. Monti and R. Simoni, *Can. J. Spectrosc.*, **27**, 171-77(1982).