Structure Change of Condensed Phosphate Ions upon Devitrification of Magnesium Metaphosphate and Calcium Magnesium Metaphosphate Glasses

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メタ燐酸マグネシウムガラスおよびメタ燐酸カルシウムマグネシウムガラスが失透する時の、縮合燐酸イオンの構造変化

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It seems magnesium metaphosphate glass containing a slight amount of ring phosphates changes into a crystalline substance known as magnesium metaphosphate by heat-treatment¹⁾. The composition of crystalline magnesium metaphosphate is magnesium tetrametaphosphate having a cyclic structure^{2),3)}. This tetrametaphosphate is considered to be an only known crystalline condensed phosphate of magnesium. Thus the devitrification process of the glass is expected to involve a drastic change in structure of the phosphate ions from a linear highpoly-form to the cyclic tetrametaphosphate.

In the present report, infra-red(IR) absorption spectra for the glasses were measured to clarify the structure-change of the phosphate anions on devitrification of MgP_2O_6 and $\text{CaMg}(\text{P}_2\text{O}_6)_2$ glasses. Detailed method of preparation of the glasses was described in the previous paper¹⁾. The IR spectra were obtained with a Hitachi EPI-2 IR spectrometer using KBr-disc technique.

The compositions of the glass samples used and the crystalline phases formed by thermal treatment of the respective glasses are given in Table 1. Figs. 1 and 2 show IR spectra for the glasses and their devitrified materials, respectively. The spectra for the $\text{CaO-P}_2\text{O}_5(\text{C-P})$ and $\text{MgO-P}_2\text{O}_5(\text{M-P})$ glasses agreed with those reported by Naruse, Abe and Inoue⁴⁾. In Fig. 1 four broad absorption bands were recognized for the three systems in common; their peaks appeared at about (a) 1300 cm^{-1} , (b) 1100 cm^{-1} , (c) 920 cm^{-1} ,

and (d) 750 cm^{-1} . Following previous researchers^{2),5)~7)}, assignment of those absorption bands could be given. The band (a) is thought to be attributable to P=O stretching (asymmetrical stretching of the middle PO_2 groups in linear chains and/or in ring phosphates), the band (b) to ionic P-O^- stretching in the middle PO_2 groups and/or the end PO_3 groups, the band (c) to P-O-H bending and/or P-O-P stretching, and the band (d) to P-O-P bending. From appearance of the bands (a) and (d), the phosphate ions in these glasses are considered to have a polymerized structure, which is either linear chains with a polymerization degree $\bar{n} \geq 3$ or cyclic form.

In Fig. 2, the broad peaks at about 900 cm^{-1}

Table 1. Composition of glass samples and crystalline phases formed on devitrification of the glasses.

Sample number	System	RO/ P_2O_5 ^{a)} (mole ratio)	Crystalline phases present in devitrified samples ^{b)}
1	$\text{CaO-P}_2\text{O}_5$	55/45	trömelite, β -calcium metaphosphate
2	"	50/50	β -calcium metaphosphate
3	"	40/60	"
4	$\text{MgO-P}_2\text{O}_5$	60/40	magnesium pyrophosphate, magnesium metaphosphate
5	"	50/50	magnesium metaphosphate
6	"	40/60	"
7	$\text{CaO-MgO-P}_2\text{O}_5$ ^{c)}	60/40	?
8	"	50/50	magnesium metaphosphate
9	"	40/60	?

a) RO: CaO , MgO or CaO+MgO

b) The glasses in the systems $\text{CaO-P}_2\text{O}_5$, $\text{MgO-P}_2\text{O}_5$ and $\text{CaO-MgO-P}_2\text{O}_5$ were heat-treated above 700° , 780°C and 755°C , respectively.

c) $\text{CaO/MgO}=1$ (mole ratio)

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Fig. 1. Infra-red absorption spectra for phosphate glass samples. The attached figure denotes sample number.

for C-P glasses and at about 920 cm^{-1} for M-P glasses diminished, and one of the characteristic peaks due to the end PO_3 groups^{2), 5), 7)} appeared at $940\sim 950\text{ cm}^{-1}$ for C-P system (Fig. 2 (1)~(3)) and at about 970 cm^{-1} for M-P system (Fig. 2 (4)). These facts suggest that a condensation-dehydration reaction was formed between the end P-O-H groups in the linear chains upon devitrification⁴⁾. The formation of the above end groups was due to the presence of residual H_2O ⁴⁾ in the glass. Thus it can be inferred that the phosphates in the starting glasses take the form of linear anion which was also detected by the paper chromatography carried out previously¹⁾.

As stated above partly, the peculiar peaks of the end PO_3 groups in the chains (near 950 cm^{-1}) and of the middle PO_2 groups (in the vicinity of 1300 cm^{-1} and $700\sim 800\text{ cm}^{-1}$) appeared in the spectra for the devitrified materials in C-P system. Therefore the crystalline phase in the specimen was viewed as a linear polyphosphate of calcium.

In the case of M-P system, the peaks attributed to the middle PO_2 groups were noticed in the spectra for the three devitrified substances (Fig. 2 (4)~(6)). The peak characteristic of the end PO_3 groups (near 970 cm^{-1}) was seen in the spectrum for the specimen with M/P=60/40, whereas such a peak was not observed for the sample with M/P=50/50 (Fig. 2 (4), (5)). Hence, it can be concluded that at least a part of the phosphates in the devitrified material with M/P=60/40 has linear chain structures and those with M/P=50/50 take cyclic forms. The spectrum for the No. 5 sample agreed exactly with that of magnesium tetrametaphosphate (Fig. 2 (5')). After all the structure-change of the phosphate anions in the MgP_2O_6 glass upon devitrification has been

Fig. 2. Infra-red absorption spectra for devitrified materials formed from the corresponding phosphate glasses. The attached figure denotes sample number. 5' is the spectrum for magnesium tetrametaphosphate quoted from ref. 2).

confirmed by means of IR spectra.

The spectrum for the devitrified sample of the $\text{CaMg}(\text{P}_2\text{O}_6)_2$ glass (Fig. 2 (8)) was similar to that for the crystallized MgP_2O_6 glass. In this case, however, several peaks were recognizable clearly. They are the small peaks at wave numbers 785, 940, 1210 cm^{-1} and 1010 cm^{-1} . The first three peaks may be due to contribution from the linear calcium polyphosphates. The last peak could not be assigned. Thus, it is stated that the phosphate ions in the devitrified material with the composition $\text{CaMg}(\text{P}_2\text{O}_6)_2$ consist of both linear and cyclic types.

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