The Consitution of $NaPO_3$-GeO_2 Melts

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The glassy and crystalline thermal products were prepared by heating a mixture of sodium phosphate glass and germanium dioxide with P/Ge ratios of 1.0—300 at 1000 °C for 3 h in a platinum crucible, and by then rapidly quenching the resulting melt. The thermal products with P/Ge ratios larger than 50 were glassy. The products with P/Ge ratios smaller than 30 were a mixture of glassy and crystalline substances, and the quantity of the glassy substance in the mixture increased with an increase in the P/Ge ratio. The crystalline substance was insoluble in water. From the results of the distribution and the average chain length of the condensed phosphates present in the glassy thermal products, it was concluded that the glass has P–O–Ge linkages and that the most reasonable chemical structure of the glass is $Ge\text{-}(\text{-}O\text{-}\underset{\displaystyle O}{\overset{\displaystyle |}{P}}\text{-})_4$. The colorimetric determination of the phosphorus and germanium contained in the crystalline thermal product showed that the P/Ge ratio of the crystalline substance is 1.3. The value of the P/Ge ratio corresponds to that of $Ge_3(PO_4)_4$.

Studies of the reaction of phosphate glass with the oxides or oxoacid salts of some elements other than phosphorus at moderately high temperatures have been carried out by several research workers. The systems studied were arsenate–phosphates,[1] silicate–phosphates,[2] vanadate–phosphates,[3] and borate–phosphates.[4,5] It was found, as a result, that the thermal products of these systems have P–O–As, P–O–Si, P–O–V, and P–O–B linkages respectively. The authors also studied the constitution of thermal products in the systems of antimonate–phosphates,[6–8] molybdate–phosphates,[9] tungstate–Phosphates,[9] aluminate–phosphates,[10] and chromate–phosphates.[11] It was concluded that they have P–O–Sb, P–O–Mo, P–O–W, P–O–Al, and P–O–Cr linkages respectively. In the present work, the glassy and crystalline thermal products in the system of $NaPO_3$–GeO_2 were investigated to obtain some information concerning the reactivity of $NaPO_3$ glass with germanium dioxide at a moderately high temperature and the structures of the thermal products.

Experimental

Preparation of the Thermal Products. A mixture of sodium phosphate glass (Graham's salt) and germanium dioxide with P/Ge ratios from 1.0 to 300 was heated in a platinum crucible at 1000 °C for 3 h. The resulting melts were quenched rapidly by placing the crucible in ice water. Sodium phosphate glass was made by heating sodium dihydrogenorthophosphate in a platinum crucible at 1000 °C for 3 h and by then quenching the melt by the same method described above.

The Solubility of the Products. About two grams of the thermal products were stirred in about 100 ml of water for 30 min at room temperature. The water-insoluble parts were then filtered off, dried, and weighed.

Paper Chromatography. The compositions of the phosphate species contained in the water-soluble part of the thermal product were determined by using one-dimensional paper chromatography. Acidic and basic developing solvents were used to separate chain phosphates (ortho-, pyro-, tri-, and high-polyphosphates) and small-ring phosphates (*cyclo*-tri- and *cyclo*-tetraphosphates) respectively.[12] About 5 μl of the mother liquor obtained by the measurement of the solubility of the thermal product was spotted onto a Toyo No. 51A filter paper (2 by 50 cm). The development was achieved at 5 °C for about 50 h. Then the filter paper was heated at 75 °C for more than 30 min in an air bath and a perchloric acid–molybdate solution was sprayed on. After drying, the paper was exposed to ultraviolet rays until blue spots appeared. The identification of each spots on the chromatograms was done by referring the spots to those of known phosphates. When the acidic developing solvent was used, the germanate ions contained in the water-soluble part of the thermal product were separated from the phosphate ions.

Colorimetric Measurement of Phosphates. Phosphates contained in the paper chromatograms were extracted with 0.1 M aqueous ammonia and determined colorimetrically by the method described in a previous paper.[6]

The Determination of the Phosphorus and Germanium Present in the Water-insoluble Thermal Product. About 0.5 g of the water-insoluble part of the thermal product was mixed with about 1.0 g of sodium carbonate, and the mixture was heated at 1000 °C for 1 h in a platinum crucible. The resulting melt was cooled rapidly in a desiccator and dissolved in 50 ml of water. About 5 μl of the sample solution was placed on a Toyo No. 51A filter paper (2 by 50 cm) and developed at room temperature for 2 days by using the acidic solvent described above. The paper was dried and sprayed a perchloric acid–molybdate solution. Then the paper was dried again and exposed to ultraviolet rays until blue spots appeared. The blue spots of phosphate and germanate were cut at the demarcation line and soaked in 10 ml of 0.1 M aqueous ammonia for 1 h. The determination of the phosphorus present in the extracting solution was made by the same method as that of a previous paper.[6] The germanium present in the extracting solution was determined colorimetrically (phenylfluorone method).

X-Ray Diffractometry. The samples were ground with an agate mortar until they could pass through a 150-mesh screen. Their X-ray diffraction diagrams were recorded on a Toshiba X-ray diffractometer, ADG-102, by means of a powder method.

Infrared Spectral Measurement. The IR spectra of the thermal products were measured with a JASCO infrared spectrophotometer, model IR-G, by using a KBr tablet method.

The Average Chain Length of Phosphates. The average chain length of phosphates present in the glassy thermal products was measured by the pH-titration method.[13,14] The effect of a germanate ion on the titration was nagligibly small.

Results and Discussion

Solubility and X-Ray Diffraction Diagrams of the Thermal Products. Table 1 shows the amount (%) of the

TABLE 1. AMOUNT OF WATER-SOLUBLE PARTS OF THE PRODUCTS AND IDENTIFICATION OF THE CRYSTALLINE PRODUCTS BY X-RAY DIFFRACTOMETRY

P/Ge	X-Ray diffraction	Water-soluble parts (%)
1.0	GeO_2, $Ge_3(PO_4)_4$	69
2.0—30	$Ge_3(PO_4)_4$	83—99
50—300	Glassy	100

water-soluble part of the thermal product and the results of the identification of crystalline thermal products by means of their X-ray diffraction patterns. The amount of the water-soluble part increased with an increase in the P/Ge ratio. The thermal products with P/Ge ratios larger than 50 were completely dissolved in water. The thermal products with P/Ge ratios from 1.0 to 30 contained crystalline substances. By referring the X-ray diffraction diagrams of the thermal products to those of ASTM cards, it was found that the thermal product with the P/Ge ratio of 1.0 contains germanium dioxide and an unknown crystalline substance, while those with the P/Ge ratios from 2.0 to 30 contain only an unknown crystalline substance. The intensity of the diffraction peaks of the products decreased with an increase in the P/Ge ratio, and the thermal products with P/Ge ratios of 20 and 30 showed only one or two weak peeks. The unknown crystalline substance was insoluble in water. According to the quantitative analysis of the phosphorus and germanium contained in the unknown crystalline substance, the P/Ge ratio of the crystal was 1.3. This value corresponds to the P/Ge ratio of germanium orthophosphate, $Ge_3(PO_4)_4$. This crystalline substance can be made by the method to be described below. The pH of an aqueous solution of sodium dihydrogenorthophosphate (30%) was adjusted to 5—7 with aqueous ammonia or aqueous sodium hydroxide, and then, under vigorous stirring, about 5 g of germanium tetrachloride was added to about 50 ml of the orthophosphate solution. The resulting precipitate was filtered off and heated at 1000 °C for 3 h in a platinum crucible. This substance gave the same X-ray diffraction diagram and P/Ge ratio as those of the unknown crystalline thermal product. Therefore, the crystalline substance may be germanium orthophosphate, $Ge_3(PO_4)_4$. The X-ray diffraction pattern of the crystalline substance is shown in Fig. 1.

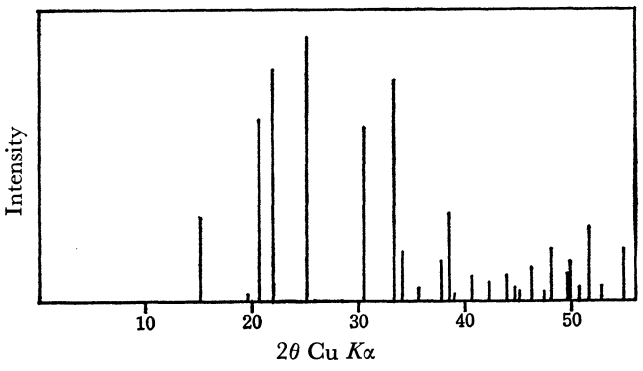


Fig. 1. X-Ray diffraction diagram of $Ge_3(PO_4)_4$.

TABLE 2. DISTRIBUTION OF PHOSPHATES OF WATER-SOLUBLE PARTS IN THE PRODUCTS

P/Ge	Ortho	Pyro	Tri	*cyclo*-Tri	*cyclo*-Tetra	Higher
1.0	42.3	45.1	9.4			3.2
2.0	44.1	45.8	7.1			3.0
3.0	19.3	61.3	10.9			8.4
5.0	3.1	47.2	3.6	2.4		43.7
7.0	1.4	30.4	6.8	2.2	1.1	58.1
10	0.4	17.8	5.0	2.8	2.1	71.9
15	0.9	11.8	3.4	3.3	2.5	78.1
20	0.3	9.1	2.6	3.3	2.4	82.3
30	0.4	6.6	2.0	3.1	2.3	85.6
50	0.6	3.7	1.4	3.4	2.6	88.3
80		2.1	1.1	3.6	2.9	90.3
100		0.8	0.9	3.6	2.4	92.3
150		0.8	0.8	3.9	3.3	91.2
200		0.4	0.4	4.2	2.7	92.3
300		0.1	0.1	4.5	2.9	92.4

Distribution of Phosphates. The results of the colorimetric determination of the phosphates (P%) contained in the water-soluble thermal products with P/Ge ratios from 1.0 to 300 are listed in Table 2. The orthophosphate content decreases with an increase in the P/Ge ratio. The pyro- and triphosphate contents show the largest value at the P/Ge ratio of 3.0 and decrease with an increase in the P/Ge ratio from 3.0 to 300. *cyclo*-Tri- and *cyclo*-tetraphosphates were usually not contained in the thermal products with P/Ge ratios of 1.0—3.0 and 1.0—5.0 respectively; if they were present, the contents of those phosphates amounted to a small percentage. The quantity of long-chain phosphates increased with an increase in the P/Ge ratio. The spot of germanate ion also appeared on the chromatograms of the sample solutions of P/Ge ratios from 1.0 to 300. The R_f value of a germanate ion was 0.50. Accordingly, the reaction of germanium dioxide with sodium phosphate glass at 1000 °C produces germanium orthophosphate and a glassy substance. In the glassy product, it could be concluded that germanium dioxide is a network-former and makes a P–O–Ge linkage. The P–O–Ge linkage may be readily hydrolyzed in a water solution to form phosphate and germanate ions, because the chain length of the phosphates contained in glassy products increases with an increase in the P/Ge ratio.

Average Chain Length of Phosphates and the Chemical Structure of Glassy Products. As is shown in Fig. 2, the average chain length of the polyphosphates of glassy products increased with an increase in the P/Ge ratio. The result is in good accordance with that of distribution of phosphates. Therefore, it can be said that the result also supports the presence of a P–O–Ge linkage in glassy products and the rapid hydrolysis of the P–O–Ge linkage in a water solution. According to the method described in previous papers,[2,6-11] the chemical structure of the glassy thermal products can be discussed by examining the relation between the average chain length of polyphosphates contained in the glassy products and the P/Ge ratio. The average chain length, $\bar{n}$, of the polyphosphates in the glass of the $NaPO_3$–GeO_2

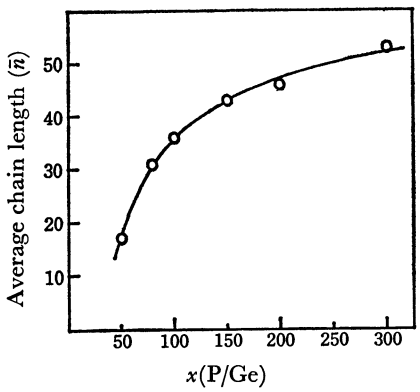


Fig. 2. Variation of average chain length of polyphosphates in the glassy thermal products with P/Ge ratios larger than 50.

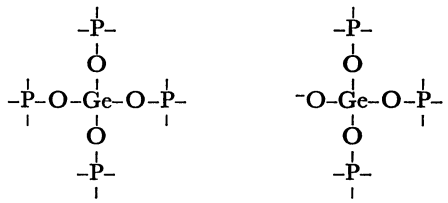
system is given by the following equation:

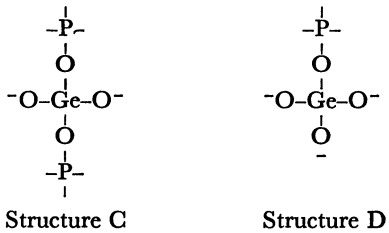
$$(\bar{n}+2)/\bar{n} = (x+y-z+fx)/x, \quad (1)$$

where x, y, and z stand for, respectively, the number of phosphorus atoms, the P–O–Ge linkages, and the Ge–O^- linkages per atom of germanium and where f is the factor shortning the chain length of the polyphos phates, given with respect to an atom of phosphorus. The f value of sodium phosphate glass was given by the following equation:

$$(\bar{n}+2)/\bar{n} = (1+f)/1. \quad (2)$$

Since the average chain length of sodium phosphate glass was 77 under the experimental conditions employed, the f value is 0.026. These four chemical structures with P–O–Ge and Ge–O^- linkages may be considered:





For each chemical structure, one can calculate the average chain length of polyphosphates present in the glass of this system by using Eq. 1. The measured and calculated average chain lengths of polyphosphates contained in the glassy products are listed in Table 3. The most reasonable chemical structure of the glassy product is Structure A, because the measured $\bar{n}$ value agrees well with the calculated one throughout the P/Ge range of 50—300.

Infrared Spectral Measurement. The infrared spectra of the starting materials and the thermal products are shown in Fig. 3. The infrared spectra of the thermal products with P/Ge ratios larger than 20 are not shown because the spectra are the same as that of sodium phosphate glass. As the P/Ge ratio becomes larger, the infrared spectrum of the thermal product gradually becomes similar to that of sodium phosphate glass. The infrared spectra of the thermal products with P/Ge

Table 3. Average chain length of polyphosphates of the thermal products with P/Ge ratios larger than 50

x (P/Ge)	$\bar{n}$ Found	$\bar{n}$ calcd by Eq. 1 (f=0.026) Structure A (y=4, z=0)	B (y=3, z=1)	C (y=2, z=2)	D (y=1, z=3)
50	17	19	30	77	—
80	31	26	39	77	2000
100	36	30	43	77	333
150	43	38	51	77	158
200	46	43	56	77	125
300	53	51	61	77	103

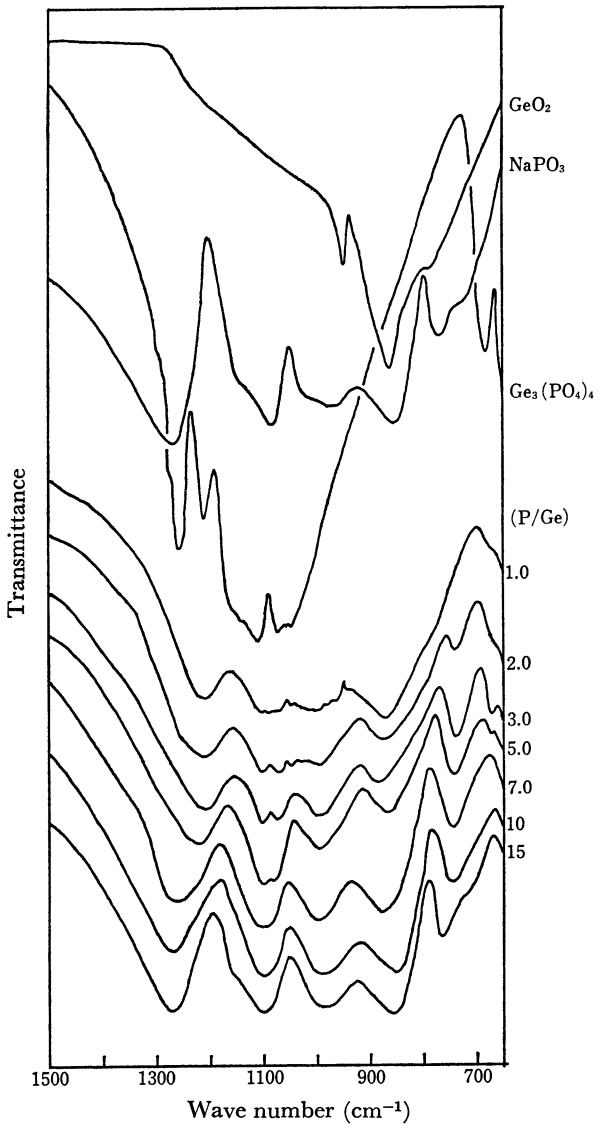
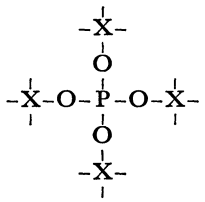


Fig. 3. IR spectra of GeO_2, $NaPO_3$, $Ge_3(PO_4)_4$, and the products with P/Ge ratios of 1.0—15.

ratios of 1.0—5.0 show absorptions (1110, 1070, and 680 cm^{-1}) attributable to germanium orthophosphate (water-insoluble part of thermal products); the absorptions are ambiguous because, as is shown in Table 1, the quantity of the water-insoluble part of the thermal products with P/Ge ratios of 1.0—5.0 is small. According to Corbridge and Lowe,[15] the absorption of sodium phosphate glass at 1270 cm^{-1} is due to P=O stretching. This absorption of thermal products gradually shifts to a lower wave number as the P/Ge ratio changes to a smaller value. It could be considered that the shift is caused by the decrease in the P=O bond strength. This could be explained as the P=O bond in sodium phosphate glass being transferred to the P⋯O⋯Ge bond by the coordination of a germanium atom. Therefore, it could be concluded that the glassy product has a four-way branching as follows:



where X stands for phosphorus or germanium. This phenomenon was also observed in the infrared spectra of the thermal products of the $NaPO_3$–Al_2O_3 system.[10]

References

1) K-H. Jost, H. Worzalla, and E. Thilo, *Z. Anorg. Allg. Chem.*, **325**, 98 (1963).
2) S. Ohashi and F. Oshima, *Bull. Chem. Soc. Jpn.*, **36**, 1489 (1963).
3) S. Ohashi and T. Matsumura, *Bull. Chem. Soc. Jpn.*, **35**, 501 (1962).
4) T. Nakamura and S. Ohashi, *Bull. Chem. Soc. Jpn.*, **40**, 110 (1967).
5) K. Honma and K. Honma, *Nippon Kagaku Kaishi*, **1972**, 856.
6) M. Watanabe, K. Tanabe, T. Takahara, and T. Yamada, *Bull. Chem. Soc. Jpn.*, **44**, 712 (1971).
7) M. Watanabe and H. Kato, *Bull. Chem. Soc. Jpn.*, **45**, 1058 (1972).
8) M. Watanabe, *Bull. Chem. Soc. Jpn.*, **46**, 2468 (1973).
9) M. Watanabe, *Nippon Kagaku Kaishi*, **1974**, 1407, 1412.
10) M. Watanabe, S. Sato, and H. Saito, *Bull. Chem. Soc. Jpn.*, **48**, 893 (1975).
11) M. Watanabe, S. Sato, and H. Saito, *Bull. Chem. Soc. Jpn.*, **49**, 3265 (1976).
12) M. Watanabe, S. Sato, and H. Saito, *Bull. Chem. Soc. Jpn.*, **48**, 896 (1975).
13) J. R. Van Wazer, E. J. Griffith, and J. F. McCulough, *Anal. Chem.*, **26**, 1755 (1954).
14) E. J. Griffith, *Anal. Chem.*, **28**, 525 (1956).
15) D. E. C. Corbridge and E. J. Lowe, *J. Chem. Soc.*, **1954**, 493, 4555.