

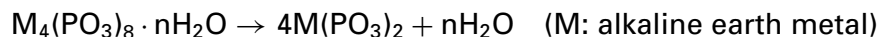
# Synthesis and thermal behaviour of alkaline earth *cyclo*-octaphosphates

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Hydrated alkaline earth *cyclo*-octaphosphates were made by adding an aqueous solution of alkaline earth chlorides into an aqueous solution of sodium *cyclo*-octaphosphate. Thermal properties of the compounds were studied by TG-DTA analysis. The water of crystallization was removed below 200 °C. The *cyclo*-octaphosphates decomposed to produce many phosphate species up to about 500 °C, and they finally reorganized to metaphosphates. The overall thermal reaction of alkaline earth *cyclo*-octaphosphates can be written by the equation.



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## 1. Introduction

Condensed phosphates are well known materials and used as food additives, detergents, chemical fertilizers, biomaterials, electroceramics, optoceramics, etc. [1–5]. Among many kinds of condensed phosphates, just a few oligophosphates (di-, tri-, tetra- [6–8], hexa- [9], *cyclo*-tri-, *cyclo*-tetra-, *cyclo*-hexa- [10–14], *cyclo*-octa- [15–18], and *cyclo*-decaphosphates [19, 20]) have been synthesized and isolated. Except for di-, tri-, *cyclo*-tri-, and *cyclo*-tetraphosphates, little is known about the chemical and physical properties of the oligophosphates. This paper describes the synthesis and thermal properties of alkaline earth *cyclo*-octaphosphates.

## 2. Experimental procedure

### 2.1. Preparation of *cyclo*-octaphosphates

Sodium *cyclo*-octaphosphate heptahydrate was made by a previous method [18]. The *cyclo*-octaphosphate (1.0 g) was dissolved in water (100 cm<sup>3</sup>) and sodium ions were removed by passing the solution through a column filled with cation-exchange resin. Magnesium chloride hexahydrate (4.44 g), calcium chloride dihydrate (1.25 g), strontium chloride hexahydrate (2.26 g), or barium chloride dihydrate (2.49 g) was dissolved in 50 cm<sup>3</sup> of water and the alkaline earth chloride solution was added into the phosphate solution with stirring. In the case of magnesium salt, the molar ratio between magnesium and a *cyclo*-octaphosphate ion was 2 to 1. In other cases, the molar ratio between a cation and a *cyclo*-octaphosphate ion was 1 to 1. Ethanol (200 cm<sup>3</sup>) was added to the mixed solution only to make magnesium *cyclo*-octaphosphate. The white precipitate produced was filtered off, washed with 75 vol % aqueous acetone, and then acetone. Then magnesium *cyclo*-

octaphosphate was dried in air for a few weeks and the other alkaline earth *cyclo*-octaphosphates were dried for one day. The yields of magnesium, calcium, strontium, and barium *cyclo*-octaphosphates were about 0.58, 0.84, 1.20, 1.21 g, respectively.

### 2.2. Chemical analysis

The determination of phosphorus and nitrogen was achieved by the Molybdenum Blue method and the Kjeldahl technique, respectively. The alkaline earth metal ions in a sample were determined by atomic absorption analysis using a Shimadzu atomic absorption spectrophotometer (AA-680).

### 2.3. X-ray diffractometry (XRD)

An XRD diagram of a powder sample was taken with nickel-filtered CuK $\alpha$  radiation using a Rigaku X-ray diffractometer, RAD-1B.

### 2.4. High-performance liquid chromatography (HPLC)

An HPLC analysis was used for separation and determination of phosphate species in a sample solution [21]. An aqueous 0.40 mol/dm<sup>3</sup> potassium chloride solution was used as an eluent and a gradient elution method was used for the separation.

### 2.5. Nuclear magnetic resonance (NMR) measurement

A <sup>31</sup>P NMR spectrum of an aqueous phosphate solution was taken using a JNM- $\alpha$ -400 instrument. Phosphoric

acid (85%) was employed as a reference with the positive shifts being down field.

## 2.6. Thermogravimetry (TG) and differential thermal analysis (DTA)

TG-DTA measurement was used to study the thermal behaviour of the products using a Rigaku TG-DTA apparatus in air with a heating rate of 5 °C/min.

## 3. Results and discussion

### 3.1. Magnesium *cyclo*-octaphosphate

#### 3.1.1. Chemical composition

The product showed only one HPLC peak in the profile. The result indicates that the product is composed of one phosphate species. The <sup>31</sup>P NMR spectrum of the product gave one singlet peak at -21.9 ppm. This means that the compound has only one kind of middle-PO<sub>4</sub> group. Chemical analysis of the product gave the contents of magnesium (9.18%), phosphorus (22.75%), and water (31.60%). The calculated contents of magnesium, phosphorus, and water for Mg<sub>4</sub>(PO<sub>3</sub>)<sub>8</sub> · 19H<sub>2</sub>O are 9.07%, 23.16%, and 31.93%, respectively. Accordingly, the product is tetramagnesium *cyclo*-octaphosphate nonadecahydrate, Mg<sub>4</sub>(PO<sub>3</sub>)<sub>8</sub> · 19H<sub>2</sub>O. XRD data of the product are given in Table I. The product was stable and did not decompose in air at room temperature.

#### 3.1.2. TG and DTA measurement

TG and DTA curves of Mg<sub>4</sub>(PO<sub>3</sub>)<sub>8</sub> · 19H<sub>2</sub>O are given in Fig. 1. The thermal products as numbered in the

TABLE I XRD data of Mg<sub>4</sub>(PO<sub>3</sub>)<sub>8</sub> · 19H<sub>2</sub>O

d value (Å)	I/I <sub>0</sub>	d value (Å)	I/I <sub>0</sub>	d value (Å)	I/I <sub>0</sub>
8.28	100	4.22	35	2.99	38
6.23	19	3.73	27	2.91	27
5.52	29	3.67	32	2.88	34
5.25	27	3.51	74	2.84	22
5.19	24	3.41	92	2.72	25
4.88	24	3.33	33	2.59	40
4.55	64	3.24	33	2.28	25
4.50	86	3.22	26	2.21	42
4.41	30				

TABLE II Analytical data of the thermal products of Mg<sub>4</sub>(PO<sub>3</sub>)<sub>8</sub> · 19H<sub>2</sub>O

Thermal product	Temp. (°C)	Wt. loss (%)	XRD	Phosphates (P%)						
				P1	P2	P3	P4	P8	cP8	Others
1	80	1.6	ST	—	—	—	—	0.9	98.4	0.7
2	190	28.2	AM	6.9	5.9	4.2	4.2	15.6	39.9	23.3
3	300	29.0	AM	4.4	10.9	12.2	12.3	12.2	10.6	37.4
*4	500	31.3	AM	4.9	3.1	1.7	2.2	—	—	88.1
*5	630	31.5	AM	—	—	—	—	—	—	—
*6	710	31.6	Mg(PO <sub>3</sub> ) <sub>2</sub>	—	—	—	—	—	—	—

\*: Thermal product containing water-insoluble phosphates.

P1, P2, P3, P4, P8, and cP8 stand for ortho-, di-, tri-, tetra-, octa-, and *cyclo*-octaphosphates, respectively.

ST: starting material, AM: amorphous.

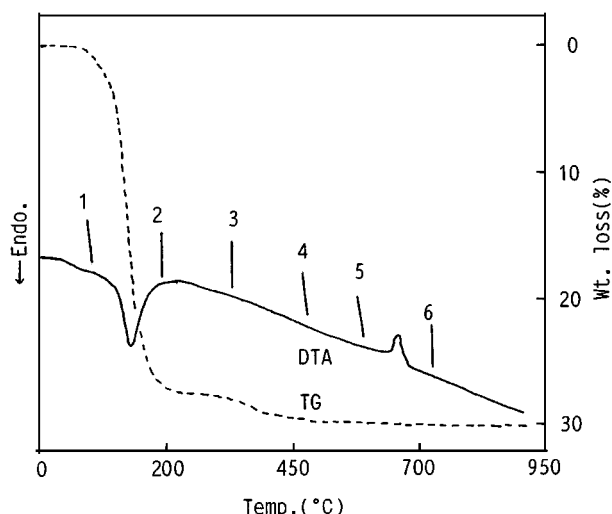
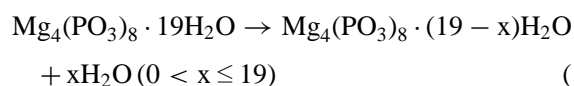
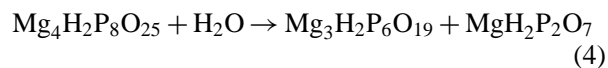
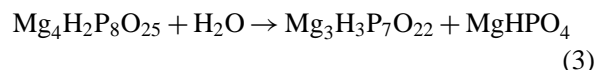
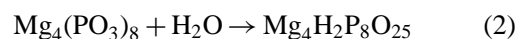


Figure 1 TG and DTA curves of Mg<sub>4</sub>(PO<sub>3</sub>)<sub>8</sub> · 19H<sub>2</sub>O.

figure were taken out of a furnace and served to further analysis to study thermal changes. The phosphate composition of the thermal products is listed in Table II together with weight loss and XRD analysis. Just a small amount of the *cyclo*-octaphosphate decomposed up to 80 °C and the XRD diagram of thermal product 1 was the same as that of the starting substance. The first large endothermic process accompanying a rapid and large weight loss was considered to be due to the release of the water of crystallization. A large amount of the *cyclo*-octaphosphate decomposed and reorganized to other phosphate species at the same time. The following thermal reactions can be written for the process.

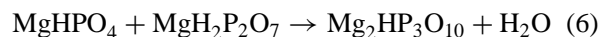
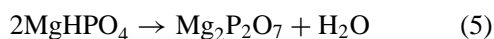


(b) Hydrolysis



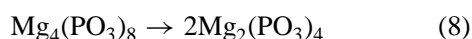
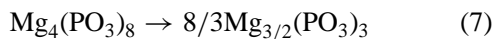
etc.

(c) Condensation



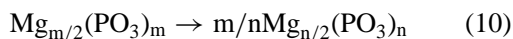
etc.

(d) Reorganization



etc.

(general equation of reorganization of *cyclo*-phosphate)



These reactions seemed to progress up to about 630 °C. The slow weight loss at about 300 to 400 °C may be caused by the condensation of the produced phosphates by hydrolysis of the *cyclo*-octaphosphate. Thermal products 2 to 5 were amorphous. Thermal product 4 contained water-insoluble phosphates and thermal product 5 was insoluble in water. After the exothermic reaction at about 650 °C, thermal product 6 showed an XRD diagram of magnesium metaphosphate and the exothermic process is due to crystallization of amorphous phosphates to the metaphosphate. Crystallinity of the thermal product increased with an increase in reaction temperature. Crystalline magnesium metaphosphate was insoluble in water. The overall thermal reaction of tetramagnesium *cyclo*-octaphosphate nonadecahydrate can be explained by the reaction.



TABLE III XRD data of  $\text{Ca}_4(\text{PO}_3)_8 \cdot 16\text{H}_2\text{O}$

d value (Å)	I/I <sub>0</sub>	d value (Å)	I/I <sub>0</sub>	d value (Å)	I/I <sub>0</sub>
10.25	12	3.84	20	2.77	34
9.69	65	3.80	29	2.70	9
9.67	51	3.58	29	2.64	18
9.17	16	3.52	11	2.51	9
9.00	100	3.37	23	2.33	12
6.58	10	3.33	17	2.97	28
4.82	14	3.20	33	2.96	9
4.48	48	3.16	14	2.91	21
4.37	20	3.13	15	2.79	18
4.11	15	2.98	18	2.77	22

TABLE IV Analytical data of the thermal products of  $\text{Ca}_4(\text{PO}_3)_8 \cdot 16\text{H}_2\text{O}$

Thermal product	Temp. (°C)	Wt. loss (%)	XRD	Phosphates (P%)						
				P1	P2	P3	P4	P8	cP8	Others
7	40	0.5	ST	—	—	—	—	—	100	—
8	110	7.8	AM	0.6	—	—	—	4.0	94.2	1.2
9	140	15.1	AM	3.5	1.0	0.8	—	11.7	74.3	8.7
10	185	20.8	AM	16.9	24.2	16.1	10.0	4.3	9.7	18.8
*11	540	26.4	UK	1.9	1.2	1.0	—	—	—	95.9
*12	560	27.5	$\text{Ca}(\text{PO}_3)_2$	—	—	—	—	—	—	—

\*: Thermal product containing water-insoluble phosphates.

P1, P2, P3, P4, P8, and cP8 stand for ortho-, di-, tri-, tetra-, octa-, and *cyclo*-octaphosphates, respectively.

ST: starting material, UK: unknown compound, AM: amorphous.

## 3.2. Calcium *cyclo*-octaphosphate

### 3.2.1. Chemical composition

Since the product gave only one HPLC peak in the profile, it was composed of one kind of phosphate. The <sup>31</sup>P NMR spectrum of the product exhibited one singlet peak at -21.6 ppm. This means that the compound has only one kind of middle-PO<sub>4</sub> group. Chemical analysis of the product gave the contents of calcium (14.18%), phosphorus (22.14%), and water (26.35%). The calculated contents of calcium, phosphorus, and water for  $\text{Ca}_4(\text{PO}_3)_8 \cdot 16\text{H}_2\text{O}$  are 14.81%, 22.96%, and 26.67%, respectively. Accordingly, the product is tetracalcium *cyclo*-octaphosphate hexadecahydrate,  $\text{Ca}_4(\text{PO}_3)_8 \cdot 16\text{H}_2\text{O}$ . XRD data of the product are given in Table III. The product was stable and did not decompose in air at room temperature.

### 3.2.2. TG and DTA measurement

TG and DTA curves of the product are shown in Fig. 2. The thermal products as numbered in the figure were taken out of a furnace and subjected to further analysis to study thermal changes. The phosphate composition of the thermal products is listed in Table IV together with weight loss and XRD analysis. Since thermal product 7 was composed of only *cyclo*-octaphosphate, the first small endothermic reaction is due to release of adsorbed water. Through the second large endothermic process at about 100 °C, a small part of the *cyclo*-octaphosphate decomposed to

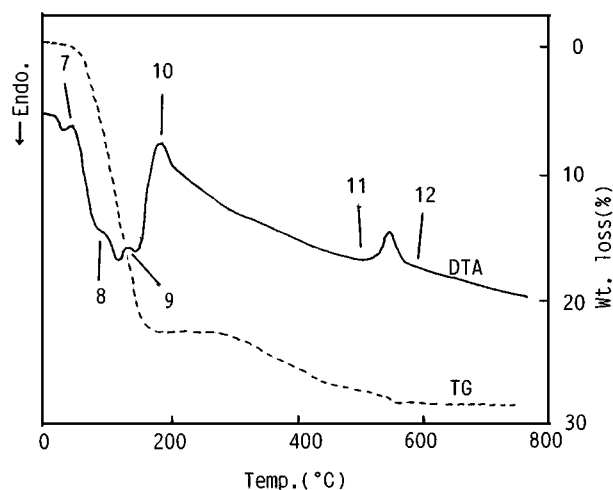


Figure 2 TG and DTA curves of  $\text{Ca}_4(\text{PO}_3)_8 \cdot 16\text{H}_2\text{O}$ .

other phosphates and a large and rapid weight loss was observed at the same time. The process was caused by elimination of the water of crystallization according to the similar process to Equation 1 and hydrolysis of the *cyclo*-octaphosphate like Equations 2 to 4 took place at the same time. In thermal products 9 and 10, the content of *cyclo*-octaphosphate decreased and those of octaphosphate and phosphates with chain length shorter than that of octaphosphate increased. Therefore, the hydrolysis similar to reactions (2) to (4) may progress at this step. A large part of thermal product 11 was insoluble in water and about 6% weight loss was observed through thermal process between 185 and 540°C. The process may be caused by the condensation of the thermally produced phosphates according to the reactions similar to Equations 5 and 6. After the exothermic reaction at about 550°C, thermal product 12 gave an XRD pattern of calcium metaphosphate (JCPDS No. 27-1273). The exothermic process is due to the reorganization of amorphous phosphates to the metaphosphate. The following overall thermal reaction can be written for the calcium *cyclo*-octaphosphate.



### 3.3. Strontium *cyclo*-octaphosphate

#### 3.3.1. Chemical composition

The product showed only one HPLC peak, implying that it is a pure compound. The <sup>31</sup>P NMR spectrum of the product gave one singlet peak at -20.9 ppm. Chemical analysis of the product gave the con-

TABLE V XRD data of Sr<sub>4</sub>(PO<sub>3</sub>)<sub>8</sub> · 14H<sub>2</sub>O

d value (Å)	I/I <sub>0</sub>	d value (Å)	I/I <sub>0</sub>	d value (Å)	I/I <sub>0</sub>
10.64	100	3.83	10	2.92	10
8.75	16	3.62	13	2.90	11
8.55	17	3.58	19	2.85	12
8.14	18	3.54	20	2.76	17
5.96	26	3.38	19	2.69	19
5.32	13	3.24	21	2.55	27
5.01	47	3.18	28	2.39	12
4.81	11	3.14	11	2.18	18
4.39	9	3.05	19		
4.30	16	2.98	14		

tent of strontium (28.20%), phosphorus (20.03%), and water (20.29%). The calculated contents of strontium, phosphorus, and water for Sr<sub>4</sub>(PO<sub>3</sub>)<sub>8</sub> · 14H<sub>2</sub>O are 28.39%, 20.09%, and 20.41%, respectively. Accordingly, the product is tetrastrontium *cyclo*-octaphosphate tetradecahydrate, Sr<sub>4</sub>(PO<sub>3</sub>)<sub>8</sub> · 14H<sub>2</sub>O. XRD data of the product are given in Table V. The product was stable and did not decompose in air at room temperature.

#### 3.3.2. TG and DTA measurement

TG and DTA curves of Sr<sub>4</sub>(PO<sub>3</sub>)<sub>8</sub> · 14H<sub>2</sub>O are given in Fig. 3. The phosphate composition of the thermal products is listed in Table VI together with weight loss and XRD analysis. Thermal product 13 showed that just a small amount of the strontium *cyclo*-octaphosphate decomposed at a temperature lower than 70°C. The first large endothermic process accompanying a rapid and large weight loss was considered to be due to the release of the water of crystallization. The hydrolysis similar to Equations 2 to 4 took place at the same time. The decomposition progressed up to 220°C. Thermal product 15 contained a small amount of condensed phosphates with chain lengths longer than that of octaphosphate and the condensation by the process like Equations 5 and 6 occurred. The weight loss at a temperature range of 220 to 500°C is due to this condensation. Thermal product 16 was amorphous and thermal product 17 gave an XRD pattern of strontium metaphosphate (JCPDS No. 44-323). The exothermic reaction at about 550°C

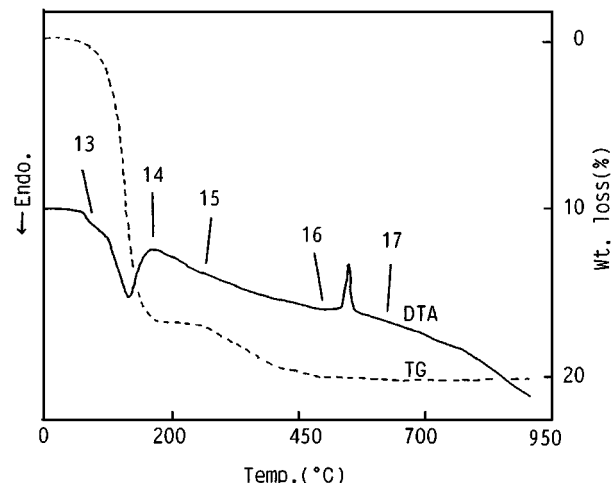


Figure 3 TG and DTA curves of Sr<sub>4</sub>(PO<sub>3</sub>)<sub>8</sub> · 14H<sub>2</sub>O.

TABLE VI Analytical data of the thermal products of Sr<sub>4</sub>(PO<sub>3</sub>)<sub>8</sub> · 14H<sub>2</sub>O

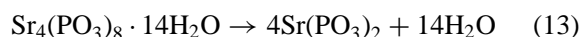
Thermal product	Temp. (°C)	Wt. loss (%)	XRD	Phosphates (P%)						
				P1	P2	P3	P4	P8	cP8	Others
13	70	2.7	ST	—	—	—	—	0.7	99.3	—
14	160	17.0	AM	9.6	6.7	4.6	4.2	12.3	38.9	23.7
15	220	17.6	AM	10.1	16.2	15.1	12.5	5.9	8.7	31.5
*16	500	19.8	AM	1.4	—	—	—	—	2.3	96.3
*17	600	20.2	Sr(PO <sub>3</sub> ) <sub>2</sub>	—	—	—	—	—	—	—

\*: Thermal product containing water-insoluble phosphates.

P1, P2, P3, P4, P8, and cP8 stand for ortho-, di-, tri-, tetra-, octa-, and *cyclo*-octaphosphate, respectively.

ST: starting material, AM: amorphous.

is caused by the crystallization process. The overall reaction like Equation 11 can be written for the thermal reaction of the strontium *cyclo*-octaphosphate.



### 3.4. Barium *cyclo*-octaphosphate

#### 3.4.1. Chemical composition

The product showed only one HPLC peak. The  $^{31}\text{P}$  NMR spectrum of the product gave one singlet peak at  $-21.0$  ppm. Chemical analysis of the product gave the content of barium (37.52%), phosphorus (17.06%), and water (19.80). The calculated contents of barium, phosphorus, and water for  $\text{Ba}_4(\text{PO}_3)_8 \cdot 18\text{H}_2\text{O}$  are 37.39%, 16.88%, and 19.60%, respectively. Accordingly, the product is tetrabarium *cyclo*-octaphosphate octadecahydrate,  $\text{Ba}_4(\text{PO}_3)_8 \cdot 18\text{H}_2\text{O}$ . XRD data of the product are given in Table VII. The product was stable and did not decompose in air at room temperature.

#### 3.4.2. TG and DTA measurement

TG and DTA curves of  $\text{Ba}_4(\text{PO}_3)_8 \cdot 18\text{H}_2\text{O}$  are given in Fig. 4. The chemical composition of the thermal products is listed in Table VIII together with weight loss and XRD analysis. Thermal products 18 and 19 showed that the barium *cyclo*-octaphosphate was thermally unstable and decomposed a little at a temperature lower than  $90^\circ\text{C}$ . The endothermic reaction accompanying a rapid weight loss at a temperature lower than  $200^\circ\text{C}$  was caused by the release of the water of crystallization and the hydrolysis processes like Equations 2 to 4 took place at the same time, because the contents of

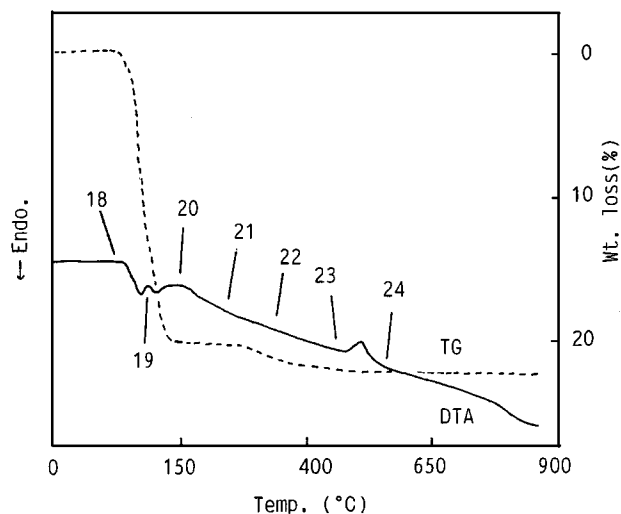


Figure 4 TG and DTA curves of  $\text{Ba}_4(\text{PO}_3)_8 \cdot 18\text{H}_2\text{O}$ .

phosphates with chain lengths shorter than that of octaphosphate in thermal products 20 and 21 increased. The condensation of phosphates produced by the thermal decomposition similar to Equations 5 and 6 may occur at a temperature higher than  $150^\circ\text{C}$ . The weight loss observed at a temperature range of  $250$  to  $300^\circ\text{C}$  was caused by the condensation, since the content of long chain condensed phosphates in thermal product 22 increased rapidly after the thermal process. Thermal product 23 was amorphous and thermal product 24 showed an XRD diagram of barium metaphosphate (JCPDS No. 43-518). The exothermic process at about  $500^\circ\text{C}$  was due to the crystallization of amorphous phosphates to the barium metaphosphate. The overall reaction like Equation 11 can be written for the thermal process of the barium *cyclo*-octaphosphate.



## 4. Summary

Hydrated alkaline earth *cyclo*-octaphosphates were made by mixing solutions of sodium *cyclo*-octaphosphate and alkaline earth chlorides. The alkaline earth *cyclo*-octaphosphates were crystalline and stable in air at room temperature. These products were thermally unstable and showed the following thermal reactions.

TABLE VII XRD data of  $\text{Ba}_4(\text{PO}_3)_8 \cdot 18\text{H}_2\text{O}$

d value (Å)	I/I <sub>0</sub>	d value (Å)	I/I <sub>0</sub>	d value (Å)	I/I <sub>0</sub>
15.38	19	4.32	9	3.16	14
14.82	100	4.12	20	3.15	9
11.78	9	4.10	34	2.99	8
11.53	20	4.08	15	2.94	30
8.70	16	3.89	16	2.93	25
7.38	26	3.78	8	2.90	13
6.84	11	3.73	11	2.66	10
5.73	7	3.61	13	2.64	29
4.92	11	3.45	9	1.72	9
4.90	9	3.25	9		

TABLE VIII Analytical data of the thermal products of  $\text{Ba}_4(\text{PO}_3)_8 \cdot 18\text{H}_2\text{O}$

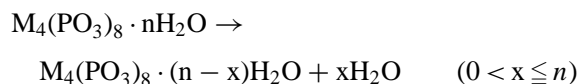
Thermal product	Temp. (°C)	Wt. loss (%)	XRD	Phosphates (P%)						
				P1	P2	P3	P4	P8	cP8	Others
18	50	0.4	AM	1.0	0.2	—	—	2.6	93.4	2.8
19	90	12.6	AM	1.3	—	—	—	5.7	89.5	3.5
20	140	20.1	AM	4.2	3.5	2.8	2.8	18.3	50.9	17.5
21	200	20.1	AM	5.2	11.1	11.2	9.7	10.2	15.7	36.9
*22	300	21.1	AM	1.9	5.1	6.7	7.1	6.4	4.9	67.9
*23	450	21.9	AM	1.2	2.0	1.8	1.4	—	—	93.6
*24	520	22.1	Ba(PO <sub>3</sub> ) <sub>2</sub>	—	—	—	—	—	—	—

\*: Thermal product containing water-insoluble phosphates.

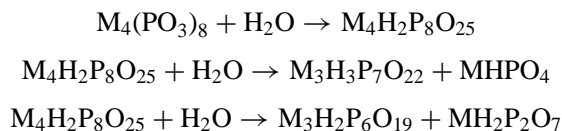
P1, P2, P3, P4, P8, and cP8 stand for ortho-, di-, tri-, tetra-, octa-, and *cyclo*-octaphosphates, respectively.

AM: amorphous.

(a) Dehydration of the water of crystallization (~200 °C)

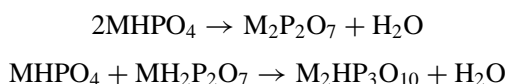


(b) Hydrolysis (~300 °C)



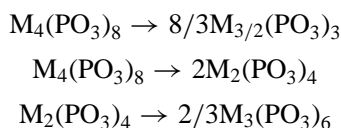
etc.

(c) Condensation (200 °C~)



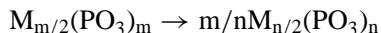
etc.

(d) Reorganization (200 °C~)

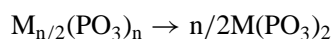


etc.

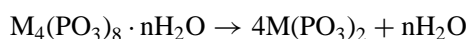
(general equation of reorganization of *cyclo*-phosphates)



(e) Crystallization of *cyclo*-phosphates to crystalline metaphosphate



(f) Overall thermal reaction



## References

1. J. R. VAN WAZER, "Phosphorus and Its Compounds," Vol. II, Interscience, New York, 1961.
2. D. E. C. CORBRIDGE, "Phosphorus," Elsevier, Amsterdam, Oxford, New York, 1980.
3. T. KANAZAWA, "Inorganic Phosphate Materials," Elsevier, Amsterdam, Oxford, New York, Tokyo, 1989.
4. A. D. F. TOY and E. N. WALSH, "Phosphorus Chemistry in Everyday Living," American Chemical Society, Washington, DC, 1989.
5. E. N. WALSH, E. J. GRIFFITH, R. N. PARRY, and L. D. QUIN, "Phosphorus Chemistry," American Chemical Society, Washington, DC, 1992.
6. O. T. QUIMBY, *J. Phys. Chem.*, **58** (1954) 603.
7. T. D. EARR, J. W. WILLIARD, and J. D. HATFIELD, *J. Chem. Eng. Data*, **17** (1972) 313.
8. K. R. WAERSTAD and G. H. MCCLELLAN, *J. Appl. Cryst.*, **7** (1974) 404.
9. M. WATANABE, N. ASAI, A. MURATA and M. SAKURAI, 8th International Symposium on Inorganic Ring Systems, Abstracts, O-26.
10. E. J. GRIFFITH and R. L. BUXTON, *Inorg. Chem.*, **4** (1965) 549.
11. M. WATANABE, K. MURATA and M. MAEDA, *Bull. Chem. Soc. Jpn.*, **61** (1988) 3877.
12. M. WATANABE, *J. Mater. Sci.*, **27** (1992) 5259.
13. M. WATANABE, M. SAKURAI, K. KATO and H. MORI, *Inorg. Mater.*, **3** (1996) 1881.
14. M. WATANABE, M. SAKURAI, K. KATO and H. MORI, *J. Mater. Sci.*, **31** (1996) 4171.
15. U. SCHULKE, *Z. Anorg. Allg. Chem.*, **360** (1968) 231.
16. M. WATANABE, T. HONDA and S. FURUTA, *Bull. Chem. Soc. Jpn.*, **64** (1991) 2918.
17. M. WATANABE, S. SATO, S. FURUTA and T. HONDA, *Phos Res. Bull.*, **1** (1991) 119.
18. M. WATANABE and T. HONDA, *Heteroatom Chem.*, **2** (1992) 587.
19. M. BAGIEU-BEUCHER, A. DURIF and J. C. GUITEL, *J. Solid State Chem.*, **45** (1982) 159.
20. U. SCHULKE, M. T. AVERBUCH-POUCHOT and A. DURIF, *Z. Anorg. Allg. Chem.*, **612** (1992) 107.
21. N. YOZA, Y. SAGARA, H. MORIOKA, T. HANDA, H. HIRANO, Y. BABA and S. OHASHI, *J. Flow Injection Anal.*, **3** (1990) 1243.

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