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Studies of the Preparation and Physical Properties of Multivalent Metal Condensed Phosphates. Part XI.[1] The Preparation of Various Aluminum Phosphates and Their Thermal Transformation

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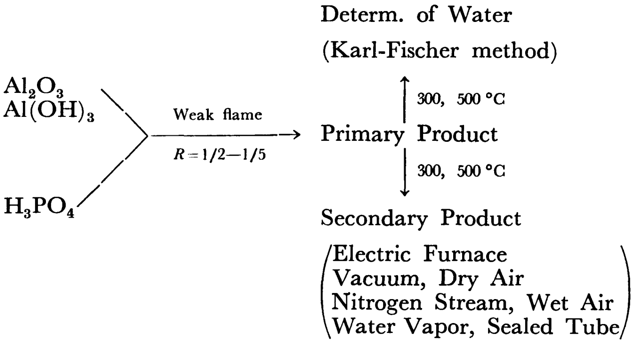
In the reaction of Al_2O_3 or $Al(OH)_3$ with phosphoric acid, the conditions of the formation of the I and II types of aluminum dihydrogen tripolyphosphate, $AlH_2P_3O_{10}$, and the A and B types of aluminum tetrametaphosphate, $Al_4(P_4O_{12})_3$, were established. The I and II types of $AlH_2P_3O_{10}$ were chiefly obtained at 300 °C; the formation of the I type predominated when the water content of the primary product was 15—30%, while the II type was more readily formed at a water content of 10—15%. Also, the I and II types were easily formed at vapor pressures of 1—5 atm. $Al_4(P_4O_{12})_3$ was produced when the water content was less than 10% or more than 30%. On the other hand, the A and B types of $Al_4(P_4O_{12})_3$ were easily formed at 500 °C; the A type was chiefly formed when the water content was below 10% or above 25%, while the B type was produced at the water content of 10—25%. The water content of the primary product is presumably due to the dehydration caused by the condensation of the P–OH. Thus water, effective for the formation of aluminum phosphates, is the structural water (P–OH). Further, the B type was liable to be formed on rapid dehydration, while the A type was more readily produced on slow dehydration. Accordingly, the formation of aluminum phosphate has been confirmed to be greatly dependent on the water content of the primary product and on the vapor pressure in the secondary heat treatment.

Although many kinds of aluminum phosphates have been discovered as minerals[2–4] and synthesized by many investigators,[5–9] their structures, methods of preparation, and physical properties are not yet well known. The existence of the A, B, C, D and E types of aluminum tetrametaphosphate, $Al_4(P_4O_{12})_3$,[10,11] and the I and II types of aluminum dihydrogen tripolyphosphate, $AlH_2P_3O_{10}$,[12–14] has already been reported by d'Yvoire, but he isolated each phosphate from its mixture by dissolution with an alkaline solution or by decantation. Therefore, their formation conditions have not yet been established. Especially, the difference between the conditions of the formation of the I and II types or those of the A and B types is not clear. According to the authors' experience, it is very difficult to establish a preparation method of aluminum phosphates, because various phosphates are formed depending on the kind of aluminum and phosphorus starting material employed, their mixing ratio, and the heating temperature.[16–19] Therefore, in this study the relationship between the water content or the dehydration velocity and the yields of aluminum phosphates was studied; the formation of phosphates in various heating atmospheres was also examined in order to investigate the influence of the vapor pressure.

Experimental

Preparation of Aluminum Phosphate. Al_2O_3 or $Al(OH)_3$ and phosphoric acid were mixed in a gold or porcelain crucible in the molar ratios Al_2O_3/P_2O_5 (R) of 1/2, 1/3, 1/4, and 1/5; the mixture was then dehydrated by heating over a weak flame with vigorous agitation to obtain a white, highly viscous product in each case. (This is designated as the primary heat treatment, giving the primary products.) A small amount (0.5—0.6 g) of the product was accurately weighed, and the content of water liberated upon heating at 300 or 500 °C was determined by the Karl-Fischer method; meanwhile, another portion was heated for 5 or 20 hr in a thermostated electric furnace, in a vacuum (0.01 mmHg), in a nitrogen stream (50 ml N_2/min, vapor pressure (vp) 0—1 mmHg), in dry air (50 ml/min, vp 0—1 mmHg), in wet air (15—20 mg H_2O/hr, vp 20—25 mmHg), in water vapor (500 g H_2O/hr, vp 760 mmHg), and in a sealed tube[20] (vp 1.5—5 atm). (This is designated as the secondary heat treatment, giving the secondary products.) The experimental method may be shown schematically as follows:



The temperature of the primary heat treatment is dependent on the aluminum materials used, their amounts, and the molar ratio R, it generally being 250—270 °C in the α-Al_2O_3—H_3PO_4 system, 140—160 °C in the γ-Al_2O_3 system, and 130—150 °C in the $Al(OH)_3$ system.

Measurement of the Dehydration Velocity. About 0.5 g of the primary product was weighed and elevated from room temperature to 500 °C at heating rates of 20, 6—7, and 0.8—1.0 °C/min, while the water content was continuously measured by the Karl-Fischer method.

Reaction of $Al(OH)_3$ or Al_2O_3 with P_2O_5. $Al(OH)_3$ or Al_2O_3 and P_2O_5 was rapidly mixed to give a molar ratio of $R=1/3$ in a dry box; the mixture was then heated in an electric furnace at 300 or 500 °C for 20 hr to form aluminum phosphates.

The aluminum phosphates thus obtained were relatively hard, but those obtained at 300 °C absorbed moisture when left in air; the phosphates were taken off the crucible as thin plates. Especially, the I type of $AlH_2P_3O_{10}$ readily absorbed moisture to form dihydrate $AlH_2P_3O_{10}\cdot 2H_2O$ and separated from the crucible easily.

Apparatus and Methods. The X-ray analysis was carried out with a Rigaku Denki Geigerflex X-ray diffractometer, using Ni filtered Cu*Kα* radiation. A Kyoto Denshi Karl-Fischer Titrator was used for the determination of water. A Rigaku Denki Diffrential Thermogravimetric Analyzer, 8002 HD, was used for the DTA and TG. The X-ray analysis, differential thermal analysis, and thermogravimetry (DTA, TG) of aluminum phosphate were carried out by the methods described in the previous papers.[18,19] The amounts of $AlH_2P_3O_{10}\cdot 2H_2O$, the II type of $AlH_2P_3O_{10}$, and the A and B types of $Al_4(P_4O_{12})_3$ formed in the secondary heat treatment were determined from the integrated intensities of their characteristic X-ray diffraction peaks; *i.e.*, $AlH_2P_3O_{10}\cdot 2H_2O$ was determined by the peak at $2\theta = 11.2°$; the II type, by that at 26.4°; the A type, by that at 20.4°; and the B type, by that at 16.2°.

Results and Discussion

Relationship Between the Yield of Aluminum Dihydrogen Tripolyphosphate and the Water Content. It is very difficult to produce the I and II types of $AlH_2P_3O_{10}$ purely, because any attempts give a mixture of $AlH_2P_3O_{10}$ and $Al_4(P_4O_{12})_3$. Therefore, for the purpose of establishing the formation conditions of the I and II types, we studied the relationship between the yields of the I and II types and the water content of the primary product. The results are shown in Fig. 1. As can be seen, the II type was obtained in a good yield when the water content of the primary product was 10—15%, while the I type was obtained at the water content of 15—30%. Also, the water content of the primary product is 8—30% in the α-Al_2O_3–H_3PO_4 system, 15—28% in the γ-Al_2O_3 system, and 15—35% in the $Al(OH)_3$ system. Therefore, the I type is most readily formed, irrespective of the aluminum materials employed, but the II type is easily produced in the α-Al_2O_3–H_3PO_4 system. The water in the primary product is considered to be composed of the structural water (P–OH), the loose water, and coordinated water, though it is found from the results of DTA and TG (Fig. 2) that the amount of the loose and coordinated water is much less than that of the structural water. This may be because the primary heat treatment was carried out at high temperatures (over 130—150 °C). In Fig. 2, the endothermic peaks with weight loss at 250—300, 360—390, and 620—630 °C are due to the dehydration caused by the condensation of the P–OH. Therefore, the formation of aluminum phosphates is confirmed to be greatly dependent on the amount of the structural water. On the other hand, $Al_4(P_4O_{12})_3$ was chiefly formed when the water content of the primary product was below 10% or above 30%, but the formation region of the A and B types was not clear at 300 °C. This may be because $Al_4(P_4O_{12})_3$ was generally formed under such special conditions as a large molar ratio and a low or high water content. $AlH_2P_3O_{10}\cdot 2H_2O$ can not be directly obtained by the secondary heat treatment at 300 °C, but when the I type of $AlH_2P_3O_{10}$ was allowed to stand in air, it readily absorbed moisture and was completely transformed into dihydrate $AlH_2P_3O_{10}\cdot 2H_2O$. Thus, the amount of the I type formed corresponds to the amount of $AlH_2P_3O_{10}\cdot 2H_2O$; accordingly, the amount of the latter is expressed as that of the former in Fig. 1. From the mixture of the composition of $R = 1/2$, $AlPO_4$ (Berlinite) was found to be formed in addition to $AlH_2P_3O_{10}$ and $Al_4(P_4O_{12})_3$, though the amount of $AlPO_4$ is omitted in Fig. 1.

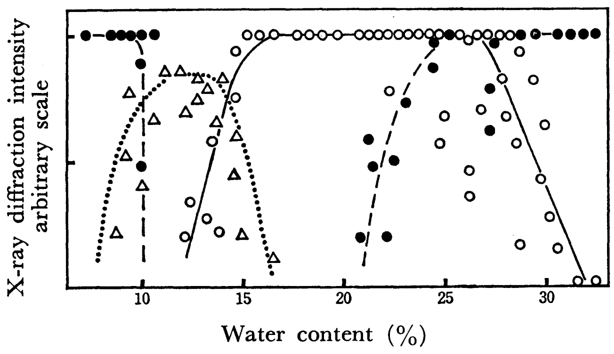


Fig. 1. Relationship between water content and the yields of various aluminum phosphates at 300 °C.
—○—: $AlH_2P_3O_{10}\cdot 2H_2O$,
···△···: II type of $AlH_2P_3O_{10}$,
—●—: Mixture of A and B types of $Al_4(P_4O_{12})_3$.

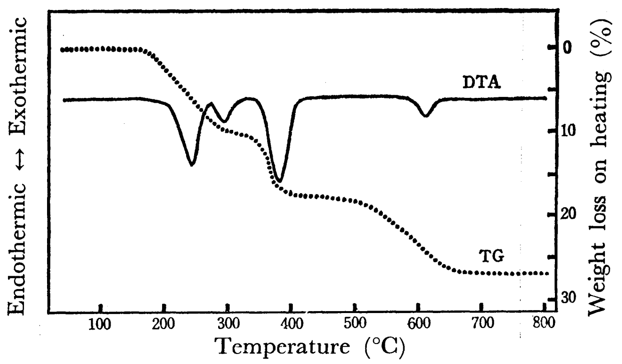


Fig. 2. DTA and TG of the primary product in the system of α-Al_2O_3–H_3PO_4.
Sample; 22 mg, Heating rate; 10 °C/min, $Al_2O_3/P_2O_5(R) = 1/3$

Relationship Between the Yield of Aluminum Tetrametaphosphate and the Water Content. Figure 3 shows the relationship between the yields of the A and B

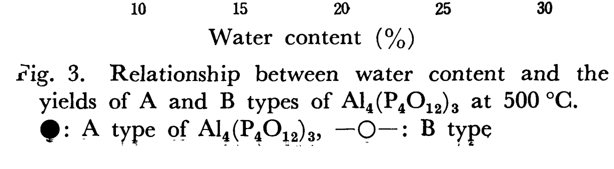


Fig. 3. Relationship between water content and the yields of A and B types of $Al_4(P_4O_{12})_3$ at 500 °C.
●: A type of $Al_4(P_4O_{12})_3$, —○—: B type

Table 1. Formation of aluminum phosphates in various heating atmospheres at 300 °C

	$\frac{1}{R}$	Water content (%)	Electric furnace		Sealed tube	Water vapor	Wet air	Nitrogen stream	Dry air	Vacuum
			5 hr	20 hr						
$Al(OH)_3$	3	18.3	I (vs)	I (vs)	I (vs)	I (s), A (w)	A (m), B (m)	I (w), A (w), B (s)	A (m), B (s)	B (vs)
		20.5	I (vs)	I (vs)	I (vs)	I (s), A (w)	A (s), B (m)	I (w), A (m), B (s)	A (w), B (vs)	B (vs)
		22.7	I (vs)	I (vs)	I (vs)	I (vs)	A (s), B (m)	I (w), A (w), B (s)	A (w), B (vs)	B (vs)
		25.0	I (vs)	I (vs)	I (vs)	I (s), A (m)	A (s), B (s)	I (w), A (w), B (vs)	B (vs)	B (vs)
	4	17.6	I (vs)	I (vs)	I (vs)	I (m), A (vs)	A (vs), B (w)	A (m), B (s)	A (w), B (s)	B (vs)
		22.5	I (vs)	I (vs)	I (vs)	I (m), A (vs)	I (w), A (s), B (w)	A (s), B (m)	A (s), B (m)	B (vs)
		23.3	I (vs)	I (vs)	I (vs)	I (m), A (vs)	I (w), A (s), B (m)	A (m), B (m)	A (m), B (s)	B (vs)
	5	22.6	I (vs)	I (vs)	I (vs)	I (w), A (vs)	A (vs), B (w)	A (w), B (vs)	A (m), B (s)	B (vs)
		26.1	I (vs), A (w)	I (vs)	I (vs)	I (w), A (vs)	A (s), B (w)	A (m), B (s)	A (s), B (s)	B (vs)
α-Al_2O_3	3	10.9	II (s), A (w)	II (s), A (w)	II (s)	II (s)	A (s), B (w)	II (w), A (m), B (m)	A (s), B (s)	B (vs)
		12.6	II (s)	II (s)	II (s)	II (s)	A (vs), B (w)	II (w), A (s), B (w)	A (m), B (s)	B (vs)
		13.8	I (w), II (s)	I (w), II (s)	I (m), II (s)	I (m), II (s)	A (vs), B (w)	II (w), A (s), B (w)	A (s), B (m)	B (vs)
		18.3	I (vs)	I (vs)	I (vs)	I (vs)	A (s), B (w)	I (w), A (m), B (m)	A (m), B (s)	B (vs)
	4	11.2	II (s)	II (s)	II (s)	II (s)	A (s), B (m)	II (m), A (w)	A (w), B (s)	B (vs)
		13.6	II (s)	II (s)	II (s)	II (m), A (w)	A (vs)	II (m), A (m), B (m)	A (m), B (s)	B (vs)
		19.3	I (vs)	I (vs)	I (vs)	I (vs)	A (s), B (s)	A (m), B (s)	A (w), B (s)	B (vs)
	5	11.4	II (s)	II (s)	II (s)	II (m), A (w)	A (vs), B (w)	A (vs)	A (vs)	A (w), B (vs)
		13.8	I (m), II (s)	I (m), II (s)	I (m), II (s)	II (m), A (m)	A (vs)	A (vs)	A (vs)	A (w), B (vs)

X-ray diffraction intensity, vs; very strong, s; strong, m; medium, w; weak, vw; very weak
Products, I; $AlH_2P_3O_{10}\cdot 2H_2O$, II; II type of $AlH_2P_3O_{10}$, A; A type of $Al_4(P_4O_{12})_3$, B; B type

Table 2. Formation of aluminum phosphates in various heating atmospheres at 500 °C

	$\frac{1}{R}$	Water content (%)	Electric furnace		Sealed tube	Water vapor	Wet air	Nitrogen stream	Dry air	Vacuum
			5 hr	20 hr						
$Al(OH)_3$	3	15.4	A (w), B (vs)	A (w), B (vs)	A (vs)	A (vs), Ber (w), Cri (m)	A (vs), B (w)	A (s), B (vs)	A (vs), B (m)	B (vs)
		19.8	A (m), B (m)	A (m), B (m)	A (vs)	A (vs), Ber (w), Cri (m)	A (vs), B (m)	A (m), B (vs)	A (vs), B (m)	B (vs)
		23.6	A (s), B (vw)	A (s), B (vw)	A (vs)	A (vs), Ber (w), Cri (m)	A (vs), B (m)	A (s), B (s)	A (vs), B (m)	B (vs)
		28.7	A (vs)	A (vs)	A (vs)	A (vs), Ber (w), Cri (m)	A (vs), B (m)	A (s), B (m)	A (vs), B (m)	B (vs)
	4	18.3	A (m), B (m)	A (m), B (m)	A (vs)	A (vs), Cri (m)	A (vs), B (w)	A (vs), B (w)	A (vs), B (w)	B (vs)
		20.1	A (s), B (w)	A (s), B (w)	A (vs)	A (vs), Cri (s)	A (vs)	A (vs), B (w)	A (vs), B (w)	B (vs)
		24.8	A (vs)	A (vs)	A (vs)	A (vs)	A (vs)	A (vs)	A (vs), B (w)	B (vs)
	5	23.7	A (vs)	A (vs)	A (vs)	A (vs), Cri (m)	A (vs)	A (vs), B (w)	A (vs), B (w)	B (vs)
		25.1	A (vs)	A (vs)	A (vs)	A (vs), Cri (w)	A (vs)	A (vs)	A (vs)	A (w), B (vs)
α-Al_2O_3	3	8.3	A (vs)	A (vs)	A (vs)	A (s), Ber (vw), Cri (m)	A (vs), B (w)	A (vs), B (w)	A (vs), B (w)	B (vs)
		10.8	A (vs)	A (vs), B (w)	A (vs)	A (s), Ber (w), Cri (m)	A (vs), B (w)	A (vs), B (w)	A (s), B (m)	B (vs)
		15.6	A (w), B (vs)	A (w), B (vs)	A (vs)	A (vs), Cri (m)	A (s), B (m)	A (s), B (m)	A (s), B (m)	B (vs)
		18.9	A (m), B (s)	A (m), B (s)	A (vs)	A (s), Ber (w), Cri (m)	A (s), B (m)	A (vs), B (w)	A (vs), B (w)	B (vs)
	4	11.3	A (s), B (w)	A (s), B (w)	A (vs)	A (s), Cri (m)	A (vs)	A (vs), B (w)	A (vs), B (w)	B (vs)
		14.6	A (m), B (s)	A (m), B (s)	A (vs)	A (vs), Cri (w)	A (vs), B (m)	A (vs), B (m)	A (s), B (w)	B (vs)
		17.1	A (m), B (vs)	A (m), B (vs)	A (vs)	A (vs), Cri (w)	A (vs), B (w)	A (vs), B (w)	A (vs), B (w)	B (vs)
	5	9.4	A (vs)	A (vs)	A (vs)	A (vs), Cri (w)	A (vs)	A (vs)	A (vs)	A (m), B (s)
		12.1	A (vs)	A (vs)	A (vs)	A (vs), Cri (w)	A (vs)	A (vs)	A (vs)	A (m), B (s)

X-ray diffraction intensity, vs; very strong, s; strong, m; medium, w; weak, vw; very weak
Products, A; A type of $Al_4(P_4O_{12})_3$, B; B type, Ber.; Berlinite, Cri.; Cristobalite type

types of $Al_4(P_4O_{12})_3$ and the water content liberated upon heating the primary product at 500 °C. The A type can be readily formed when the water content of the primary product is below 10% or above 25%, while the B type is obtained at a water content of 10—25%. The results show that the region of formation of the B type is more limited than that of the A type, it consequently being very difficult to prepare the pure B type. The authors repeated the experiment by this procedure 500—600 times, but only in 2—3% of the experiments could the pure B type be obtained, the product in most cases being a mixture of the A and B types. The A type was more likely to be obtained when the molar ratio, R, was low ($R=1/4$—$1/5$), that is, at larger amounts of phosphoric acid. The I and II types of $AlH_2P_3O_{10}$ were not formed at all at 500 °C, possibly because of the thermal transformation of the I and II types into $Al_4(P_4O_{12})_3$ at this temperature. The thermal transformation of the I and II types will be considered in detail latter.

Relationship Between the Formation of Aluminum Tetrametaphosphate and the Dehydration Velocity. As has been described above, the formation of $Al_4(P_4O_{12})_3$ was greatly affected by the water content of the primary product. The rate of dehydration of the primary product was examined in order to investigate the influence of dehydration in the preparation of the A and B types of $Al_4(P_4O_{12})_3$, using several samples with equal water contents. Figure 4 shows the relationship between the heating temperature and the weight loss (the degree of dehydration) at the heating rate of 6—7 °C/min. The ultimate weight loss of each sample was about 24—25%. Naturally, the amount of product may differ with the water content of the primary product, but in the primary product containing same water content it is also seen that the higher the dehydration velocity, the more readily the B type is formed, whereas the slower the dehydration velocity, the more A type is produced. Almost the same results were obtained at heating rates of 0.8—1.0 and 20 °C/min. About 70 to 75% of the $Al_4(P_4O_{12})_3$ prepared in this experiment gave the A or B types or a mixture of the A and B types, according to dehydration velocity.

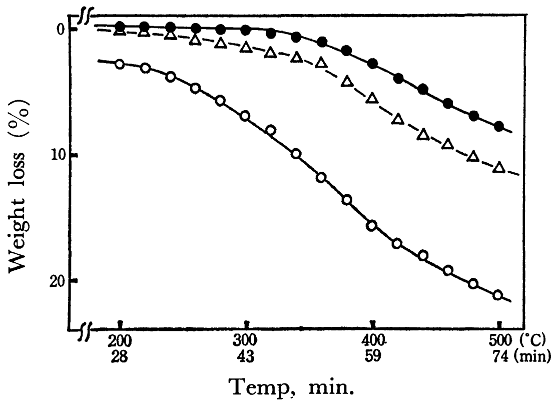


Fig. 4. Relationship between the formation of $Al_4(P_4O_{12})_3$ and dehydration velocity.
—●—: A type of $Al_4(P_4O_{12})_3$,
--△--: Mixture of A and B types
—○—: B type
Heating rate; 6—7 °C/min
Final weight loss; 24—25%

Preparation of Aluminum Phosphate in Various Heating Atmospheres. The relationship between the heating atmosphere and the products obtained at 300 °C is shown in Table 1. On heating in an electric furnace, the I type of $AlH_2P_3O_{10}$ was the product chiefly formed when the water content was 15—30%, while the II type was obtained at a water content of 10—15%. This is in good agreement with the above-mentioned results. A comparison of the products obtained in dry air, a nitrogen stream, wet air, water vapor, and in a sealed tube shows that both the I and II types are readily formed by heating the primary product in atmospheres containing much water, while neither of them is produced at all in dry air. In particular, it was proved that the type of product obtained in a sealed tube is dependent entirely on the water content of the primary product. Thus, it is clear that a high vapor pressure is required for the formation of the I and II types. On the contrary, on heating in a vacuum, no $AlH_2P_3O_{10}$ was obtained at all, and only the B type was formed. This shows that the B type is readily formed by rapid dehydration, as has been described above. The product becomes hygroscopic as the molar ratio R decreases ($R=1/4$—$1/5$), that is, with an increase in the amount of phosphoric acid. The relationship between the heating atmosphere and the products formed at 500 °C is given in Table 2. In both the α-Al_2O_3–H_3PO_4 and $Al(OH)_3$–H_3PO_4 systems at $R=1/3$, although some difference in products was observed according to the water content of the primary product, a mixture of the A and B types of $Al_4(P_4O_{12})_3$ was the product chiefly formed, regardless of the heating atmosphere; this shows that the kind of atmosphere had very little influence here. On the contrary, only the A type was obtained in a sealed tube, irrespective of the aluminum materials used, the molar ratio, and the water content. This may be because of the difficulty of the evaporation of water, *i. e.*, by the very low dehydration velocity. The formation of a mixture of the A type and $AlPO_4$ (berlinite and cristobalite type) in an atmosphere of water vapor can be interpreted in terms of the evaporation of the white P_2O_5 fumes caused by the flow of water vapor. The complete absence of the formation of the B type may also be due to the low dehydration velocity in water vapor, such as in a sealed tube. On the other hand, only the B type was obtained in a vacuum, *i. e.*, under conditions of rapid dehydration. The formation of the A type became dominant with a decrease in the molar ratio ($R\leqq 1/5$), regardless of the heating atmosphere, except in a vacuum, where the B type was still the product chiefly formed. The conditions for the formation of the A and B types could not be determined at 300 °C, but were clearly distinguished at 500 °C. No I or II type was formed at all at 500 °C. At $R=1/2$, a mixture of $Al_4(P_4O_{12})_3$ and $AlPO_4$ (berlinite and cristobalite type) was formed in any heating atmosphere. $AlPO_4$ (berlinite) was formed more readily in the $Al(OH)_3$–H_3PO_4 system than in the α-Al_2O_3–H_3PO_4 system. This may be explained in terms of the higher reactivity of $Al(OH)_3$ than that of α-Al_2O_3 with phosphoric acid.

Reaction of α-Al_2O_3 or $Al(OH)_3$ with P_2O_5. Reactions in the systems of α-Al_2O_3–P_2O_5 and $Al(OH)_3$–P_2O_5 were carried out in order to investigate the preparation of aluminum phosphate in a much lower water content. At 500 °C, almost only the A type was formed in the α-Al_2O_3–P_2O_5 system, but the A type was contaminated by the B type in the $Al(OH)_3$–P_2O_5 system. This may be because of the water contained in $Al(OH)_3$. Thus, these experimental results show that the A type is liable to be produced in the absence of water.

Thermal Transformation of Aluminum Dihydrogen Tripolyphosphate. Although the present authors have already reported data on the thermal transformation of $Al_4(P_4O_{12})_3$,[21] little is yet known about that of $AlH_2P_3O_{10}$. The results of the DTA and TG of $AlH_2P_3O_{10}\cdot 2H_2O$ and the II type are shown in Fig. 5. For $AlH_2P_3O_{10}\cdot 2H_2O$, an endothermic reaction with a weight loss of $2H_2O$ was observed at about 150—160 °C; further, another endothermic reaction with a weight loss of the structural water occurred at about 520—530 °C, and the B type was formed. For the II type, an endothermic reaction occurred at 560—570 °C, and losing its structural water, the II type was transformed into a mixture of the A and B types of $Al_4(P_4O_{12})_3$. The determination of the water by the Karl-Fischer method proved that the weight loss seen in the TG curve was caused only by the loss of water. Figures 6 and 7 show the results obtained on heating the I and II types in air at 400—1200 °C for 5 hr. The I type was transformed into the D type of $Al_4(P_4O_{12})_3$ when heated at 450—500 °C; into the B type, at 500—800 °C, and into the A type, above 900 °C. The thermal transformation from the D type to the B type or from the B type to the A type could not be confirmed by the DTA method. On the other hand, the thermal transformation of the II type was quite different from that of the I type, a mixture of the A and B types being directly obtained with no intermediate D type. The B type was readily obtained at 500 to 800 °C, but it was always contaminated by the A type; while only the A type was formed above 900 °C. Further, both the I and II types were vitrified by heating at 1200 °C for 5 hr. From these results, it may be concluded that the thermal transformation of the I and II types and of $AlH_2P_3O_{10}\cdot 2H_2O$ heated in air occurs as follows:

$$AlH_2P_3O_{10}\cdot 2H_2O \xrightleftharpoons{150\text{—}160\,^\circ C} AlH_2P_3O_{10}\ \text{I type}$$

$$\xrightarrow{450\text{—}500\,^\circ C} Al_4(P_4O_{12})_3\ \text{D type} \xrightarrow{500\,^\circ C} \text{B type} \xrightarrow{900\,^\circ C}$$

$$\text{A type} \xrightarrow{1200\,^\circ C} \text{Metaphosphate glass}$$

$$AlH_2P_3O_{10}\ \text{II type} \xrightarrow{560\text{—}570\,^\circ C} \text{A} + \text{B type} \xrightarrow{900\,^\circ C}$$

$$\text{A type} \xrightarrow{1200\,^\circ C} \text{Metaphosphate glass}$$

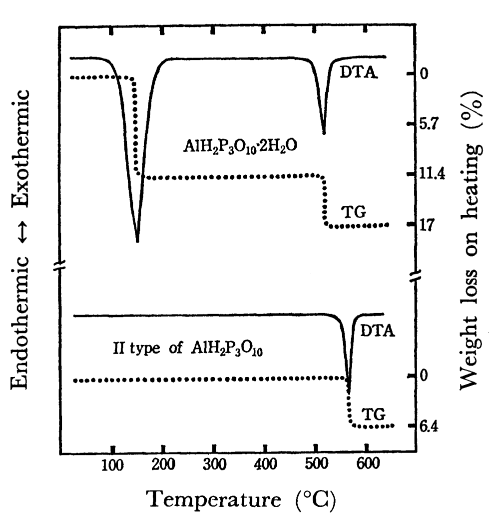


Fig. 5. DTA and TG of aluminum dihydrogen tripolyphosphate.
Sample; 30 mg, Heating rate; 10 °C/min.

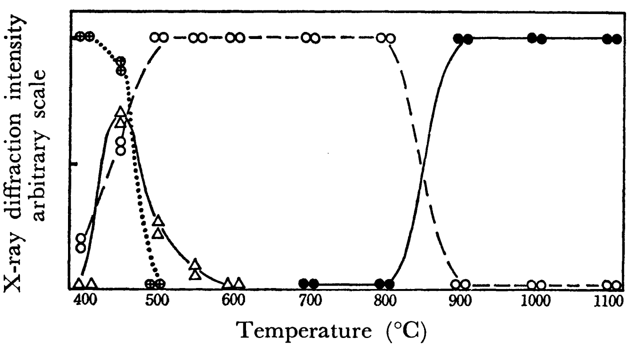


Fig. 6. Thermal transformation of I type of $AlH_2P_3O_{10}$.
···⊕···: I type of $AlH_2P_3O_{10}$, —△—: D type, —○—: B type, —●—: A type

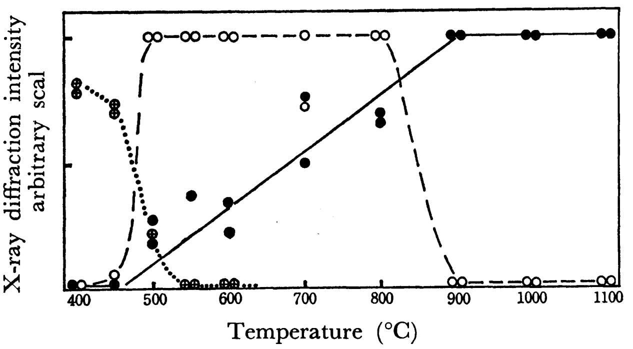


Fig. 7. Thermal transformation of II type of $AlH_2P_3O_{10}$.
···⊕···: II type of $AlH_2P_3O_{10}$, --○--: B type, —●—: A type.

Conclusions

The experimental results can be summarized as follows:

1) The formation of aluminum phosphates is greatly dependent on the water content of the primary product and on the vapor pressure in the secondary heat treatment.

2) The water effective in the formation of phosphates is that resulting from the dehydration caused by the condensation of the P–OH.

3) The I and II types of $AlH_2P_3O_{10}$ are produced

by heating the primary product at 300 °C; the I type can be most readily obtained when the water content of the primary product is 15—30%.

4) The II type is readily formed when the water content is 10—15%. Both the I and II types are formed under the conditions of a high vapor pressure.

5) $Al_4(P_4O_{12})_3$ is chiefly formed at a heating temperature above 500 °C. The A type is easily obtained when the water content is below 10% or above 25%.

6) The B type is formed at a water content of 10—25%.

7) $AlH_2P_3O_{10}\cdot 2H_2O$ undergoes the following thermal transformation in air: $AlH_2P_3O_{10}\cdot 2H_2O \rightleftarrows$ I type → D type → B type → A type → Metaphosphate glass.

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