CHEMISTRY LETTERS, pp. 435-438, 1974. Published by the Chemical Society of Japan

STUDIES OF THE PREPARATION AND PHYSICAL PROPERTIES OF MULTIVALENT METAL CONDENSED PHOSPHATES. X.[1] PREPARATION AND THERMAL TRANSFORMATION OF TITANIUM(III) TETRAMETAPHOSPHATE

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Titanium tetrametaphosphate $Ti_4(P_4O_{12})_3$ is readily formed in a nitrogen stream or vacuum. It is found from the X-ray diffraction pattern that $Ti_4(P_4O_{12})_3$ is isomorphous with the A type of aluminum tetrametaphosphate $Al_4(P_4O_{12})_3$. $Ti_4(P_4O_{12})_3$ shows a large exothermic peak at 250 ~ 400°C and a small endothermic peak at 650 ~ 660°C, and this compound is gradually converted at 250 ~ 400°C to give titanium pyrophosphate TiP_2O_7 and P_2O_5.

Although various studies have been carried out on titanium(IV) phosphate,[2~4] little has been reported on the preparation, structure, and thermal transformation of $Ti_4(P_4O_{12})_3$; the report by Liebau and Williams[5] is the only one on the preparation and structure of this compound. However, it was very difficult to form $Ti_4(P_4O_{12})_3$ purely by their method. Appropriate conditions of formation for this compound is not yet fully revealed. Therefore, in the present experiment we have studied the formation conditions of $Ti_4(P_4O_{12})_3$, for example molar ratio TiO_2/P_2O_5 (R) in the starting material, heating temperature and heating atmosphere and investigated its composition and thermal transformation by X-ray analysis, infrared absorption spectroscopy, and simultaneous measurements of differential thermal analysis and thermogravimetry (DTA, TG). To study the similarity in structures of $Ti_4(P_4O_{12})_3$ and A type of $Al_4(P_4O_{12})_3$, we have also compared X-ray diffraction pattern and IR spectrum of $Ti_4(P_4O_{12})_3$ with those of $Al_4(P_4O_{12})_3$.

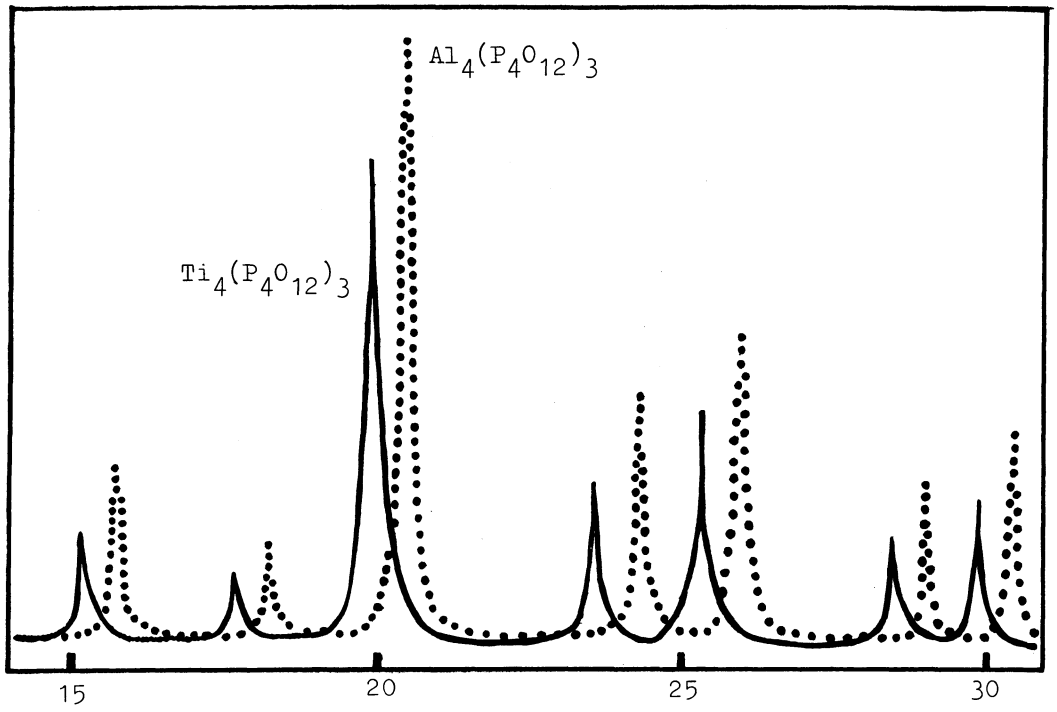

Fig. 1. X-ray diffraction patterns of titanium(Ⅲ) and aluminum tetrametaphosphates

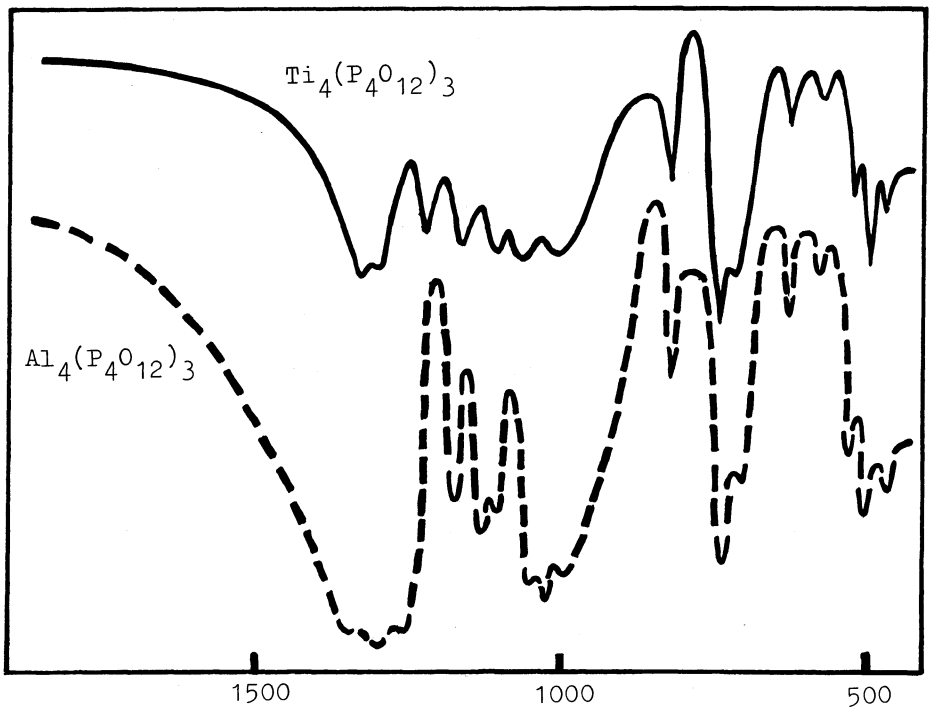

Fig. 2. IR spectra of titanium(Ⅲ) and aluminum tetrametaphosphates

Titanium metal and phosphoric acid were mixed in a porcelain crucible in a molar ratio R of 1/1 ~ 1/5, and the mixture was dehydrated by heating over a weak flame under vigorous agitation. The reaction was vigorous with foaming and the evolution of hydrogen. This dehydration product was further heated in air, nitrogen stream (50 ml/min) or vacuum(0.01 mm Hg) at 300 ~ 700 °C for 5 hrs. Though a mixture of $Ti_4(P_4O_{12})_3$ and TiP_2O_7 was usually given when the dehydration product was heated in air, $Ti_4(P_4O_{12})_3$ was purely formed when the dehydration product of R = 1/3 ~ 1/4 was heated in a nitrogen stream or vacuum at 500 °C for 5 hrs. Also, chiefly TiP_2O_7 was obtained irrespective of the heating atmosphere when molar ratio R was larger than 1/3. $Ti_4(P_4O_{12})_3$ purely formed was rapidly washed to remove excess phosphoric acid, with distilled water through which nitrogen gas had been passed, then dried at 80 °C for 24 hrs.

Fig. 1 shows that the X-ray diffraction peaks of $Ti_4(P_4O_{12})_3$ are shifted to lower diffraction angles than those of A type of $Al_4(P_4O_{12})_3$, which suggests that $Ti_4(P_4O_{12})_3$ has longer crystallographic axes than A type of $Al_4(P_4O_{12})_3$ has (ion radii of Ti^{3+} = 0.76 Å, Al^{3+} = 0.50 Å).

Fig. 2 shows the infrared absorption spectra of $Ti_4(P_4O_{12})_3$ and $Al_4(P_4O_{12})_3$. Like the aluminum compound, $Ti_4(P_4O_{12})_3$ shows a doublet P-O-P (asymmetric bending) absorption at 1000 ~ 1100 cm^{-1} and two P-O-P (symmetric bending) absorption peaks near 803 and 730 cm^{-1}.

DTA and TG of $Ti_4(P_4O_{12})_3$ in Fig. 3 show a large exothermic peak at 250 ~ 400 °C with an increase in weight. At over 400 °C, the weight begins to decrease gradually and is almost constant with weight loss of about 22 % at about 660 °C. A small endothermic peak is noticed about 650 ~ 660 °C. When differential thermal analysis of $Ti_4(P_4O_{12})_3$ was carried out in a nitrogen stream (25 ml/min), neither the exothermic nor endothermic peak described above was observed, and no change in weight was seen. The results of X-ray analysis indicate that the blue color of $Ti_4(P_4O_{12})_3$ disappears and white colored TiP_2O_7 is formed at temperature above point B (500 °C) in Fig. 3. The product heated at the temperature of point A (370 ~ 390 °C) shows large hygroscopicity if left in the air . From these results we can say that the following reaction takes place when $Ti_4(P_4O_{12})_3$ is heated in air;

$$Ti_4(P_4O_{12})_3 + O_2 \xrightarrow[\text{in air}]{370 \sim 390\ ^\circ C} 4\ TiP_2O_7 + 2\ P_2O_5$$

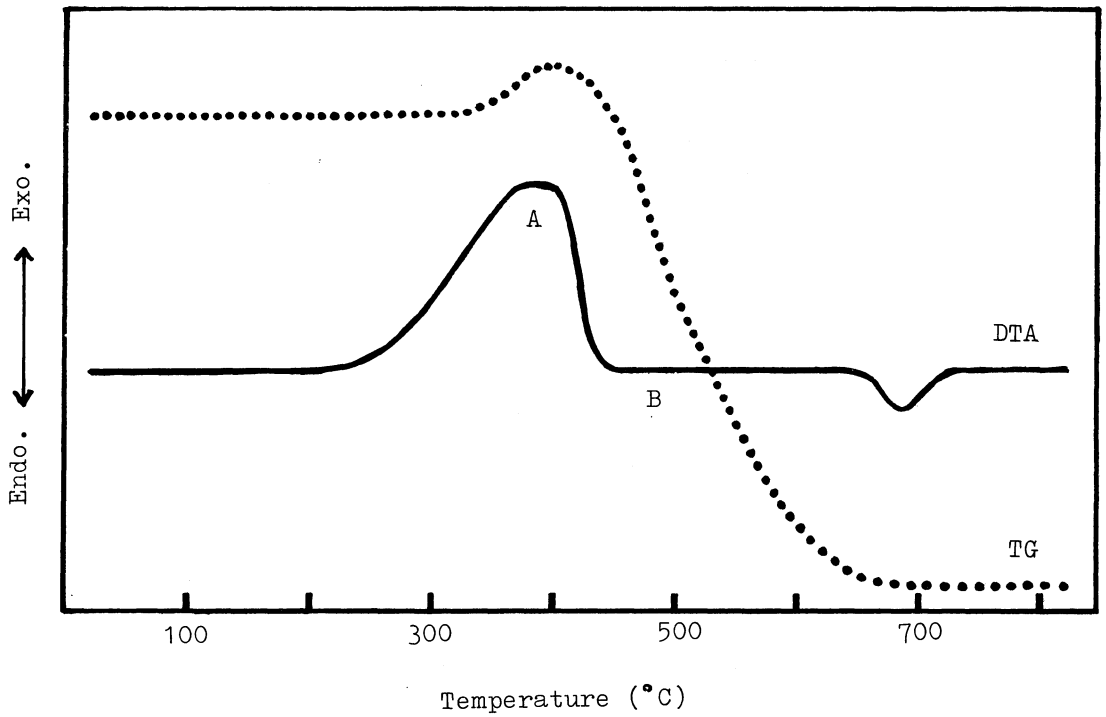

Fig. 3. DTA and TG of titanium tetrametaphosphate

The oxidation of $Ti_4(P_4O_{12})_3$ begins gradually at 250~400°C to give TiP_2O_7 and P_2O_5. On the other hand, A type of $Al_4(P_4O_{12})_3$ does not show any thermal change at all up to 1000°C.

References

1) For part IX of this series, M. Tsuhako, I. Motooka, and M. Kobayashi, Nippon Kagaku Zasshi, in press.
2) G. R. Levi and G. Peyronell, Z. Krist., 92, 190 (1935).
3) D. E. Harrison and F. A. Hummel, J. Amer. Ceram. Soc., 42, 487 (1959).
4) E. Steger and G. Leukroth, Z. anorg. allgem. Chem., 303, 196 (1960).
5) F. Liebau and H. P. Williams, Angew. Chem., 76, 303 (1964).

(Received February 18, 1974)