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STUDIES ON THE PREPARATION AND PHYSICAL PROPERTIES OF MULTIVALENT METAL CONDENSED PHOSPHATES. XII.[1)]

PREPARATION OF VARIOUS CERIUM PHOSPHATES

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$CePO_4$, CeP_2O_7, $Ce(PO_3)_4$, and CeP_5O_{14} were chiefly obtained by the reaction of CeO_2 with phosphoric acid; while $CePO_4 \cdot 0.5H_2O$, $CePO_4$, $Ce(PO_3)_3$, and CeP_5O_{14} by the reaction of $CeCl_3$ with phosphoric acid. The crystal of $Ce(PO_3)_4$ was isomorphous with that of $U(PO_3)_4$, thus $Ce(PO_3)_4$ must be a novel tetravalent cerium metaphosphate. The existence of two kinds of cerium metaphosphate, $Ce(PO_3)_4$ and $Ce(PO_3)_3$, was confirmed in this study.

Rare earth phosphates have recently become an object of attention as laser materials and various studies on them have been published.[2 — 14)] Among these there have been reports on the synthesis of rare earth phosphates, various compounds having been obtained according to the conditions of preparation. However, there have yet been few reports[15 — 17)] of systematic and fundamental studies on the conditions of the formation of individual rare earth phosphates. We report here an investigation of the formation of cerium phosphates by the reaction of CeO_2 or $CeCl_3$ with phosphoric acid, in the course of which study a hitherto unreported compound, tetravalent cerium metaphosphate was successfully synthesized.

The following experimental procedure was used. CeO_2 or $CeCl_3$ was mixed with 85 % phosphoric acid in a gold or porcelain crucible in an atomic ratio P/Ce (R) of 1 — 50, and the mixture was dehydrated by heating over a small flame. On heating, the mixture gradually became viscous, and finally turning into a yellow, transparent liquid. On heating this liquid in an electric furnace at 300 — 800°C for 20 hr — 7 days, cerium phosphates were obtained. The amounts of various cerium phosphates resulting from this treatment were determined from the integrated intensities of their characteristic X-ray diffraction peaks. Thus, orthophosphate, $Ce(III)PO_4$, was determined from the peak at 2θ = 26.9° (d = 3.31 Å); pyrophosphate, $Ce(IV)P_2O_7$, from that at 20.5° (4.33 Å); metaphosphate, $Ce(IV)(PO_3)_4$, from that at 22.0° (4.04 Å); and ultraphosphate, $Ce(III)P_5O_{14}$, from that at 23.7° (3.75 Å).

As an example of the results, the relationship between the amounts of various cerium phosphates formed at 700°C and atomic ratio R in the system CeO_2 — H_3PO_4 is shown in Fig. 1. At 700°C, $CePO_4$, CeP_2O_7, $Ce(PO_3)_4$, and CeP_5O_{14} were the compounds predominantly formed at R values of about 1, 2, 2 — 6, and above 10, respectively.

On the other hand, at a heating temperature below 500°C, the formation of CeP_2O_7 was predominant in the range R = 1 — 4, and that of $Ce(PO_3)_4$ at R values above 4; while at R values between 6 and 8 $Ce(PO_3)_4$ was the sole product. From these result it is clear that the CeO_2 — H_3PO_4 system gives phosphates of trivalent and tetravalent cerium. The heating of mixtures of CeO_2 and phosphoric acid at 800°C or above gave trivalent cerium metaphosphate, $Ce(PO_3)_3$, in small yield.

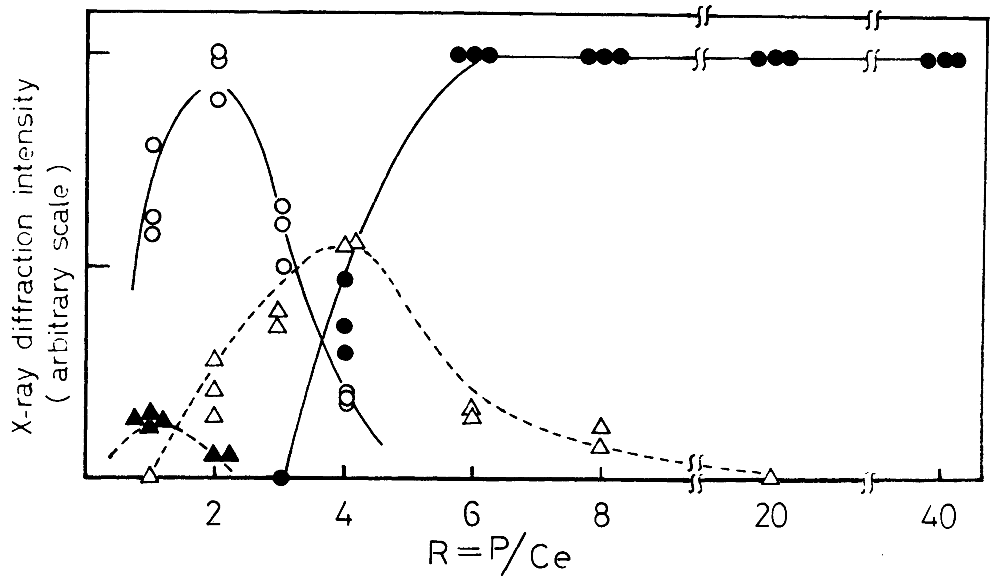

Fig. 1 Relation between atomic ratio P/Ce (R) and yields of cerium phosphates formed at 700°C
--▲-- $CePO_4$, -○- CeP_2O_7, --△-- $Ce(PO_3)_4$, -●- CeP_5O_{14}

On the contrary, the products obtained from the system $CeCl_3$ — H_3PO_4, though they varied according to the atomic ratio R and the heating temperature, were generally $CePO_4$, $CePO_4 \cdot 0.5H_2O$, $Ce(PO_3)_3$, and CeP_5O_{14}. Neither CeP_2O_7 nor $Ce(PO_3)_4$ were formed at all by the system.

Though $CePO_4$, CeP_2O_7, $Ce(PO_3)_3$, and CeP_5O_{14} are known compounds, 8, 18, 19) there have as yet been no reports on $Ce(PO_3)_4$. It was ascertained by X-ray powder diffraction that $Ce(PO_3)_3$ is isomorphous with $La(PO_3)_3$, $Pr(PO_3)_3$, $Nd(PO_3)_3$, $Sm(PO_3)_3$ etc. 15, 17, 18); while $Ce(PO_3)_4$ is isostructural with $U(PO_3)_4$, $Th(PO_3)_4$, and $Pu(PO_3)_4$. 20 — 22) It was further shown that the crystals of both $Ce(PO_3)_3$ and $Ce(PO_3)_4$ are orthorhombic. 15)

The X-ray diffraction patterns and IR spectra of $Ce(PO_3)_4$ and $Ce(PO_3)_3$ are shown in Figs. 2 and 3. X-ray diffraction pattern of $U(PO_3)_4$ are also given for reference. The fluorescent X-ray spectrometry of $Ce(PO_3)_4$ confirmed that the ratio of P to Ce was 4.

It was thus concluded from above results that two kinds of cerium metaphosphate, namely $Ce(PO_3)_3$ and $Ce(PO_3)_4$, can be obtained from the $CeCl_3$ — H_3PO_4 and CeO_2 — H_3PO_4 systems; and isomorphism with $U(PO_3)_4$ showed that $Ce(PO_3)_4$ must be a novel tetravalent cerium metaphosphate.

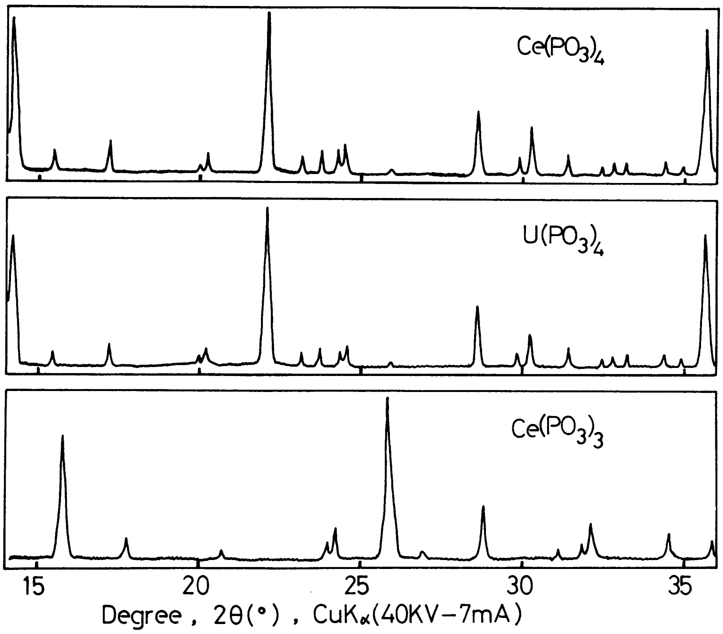

Fig. 2 X-ray diffraction patterns of $Ce(PO_3)_4$, $U(PO_3)_4$, and $Ce(PO_3)_3$

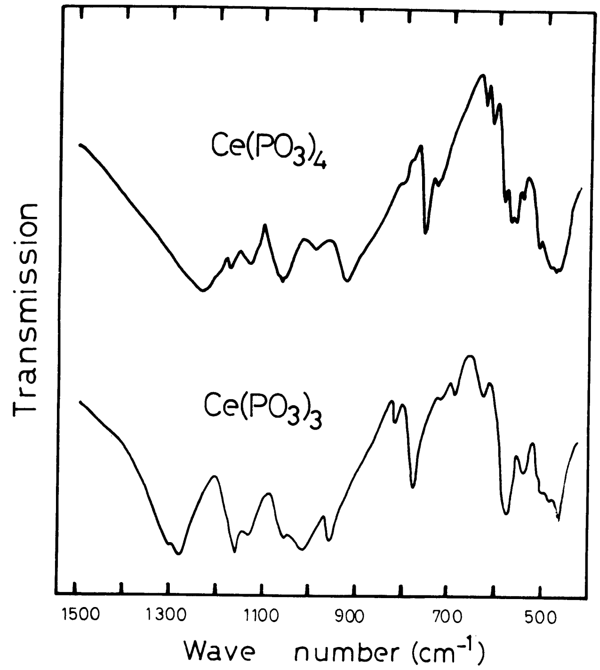

Fig. 3 IRS of cerium metaphosphates

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