Conditions of the Formation of Rare Earth Phosphates and the Colors of Their Powders

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Rare earth oxides, such as La_2O_3, Pr_6O_{11}, Nd_2O_3, and Sm_2O_3, can react with phosphoric acid to give four kinds of rare earth phosphates (orthophosphates $LnPO_4 \cdot 0.5H_2O$ and $LnPO_4$, *catena*-polyphosphates $Ln(PO_3)_3$ and ultraphosphates LnP_5O_{14}), while in the reaction of CeO_2 with phosphoric acid there are formed five kinds of phosphates (orthophosphate $CePO_4$, pyrophosphate CeP_2O_7, two types of *catena*-polyphosphate $Ce(PO_3)_3$ and $Ce(PO_3)_4$, and ultraphosphate CeP_5O_{14}). The formation of these products in the CeO_2–H_3PO_4 system are notably different from these in other systems, showing that cerium(III) phosphates as well as cerium(IV) phosphates can exist stably. It can be seen from the X-ray diffraction patterns that each corresponding phosphate (ortho, *catena*-poly, and ultraphosphates) of lanthanum, cerium(III), praseodymium, neodymium, and samarium is isomorphous. This may be caused by the facts that the valencies of all these metals are +3 and that their ionic radii are almost equal to one another (La(III) 1.06 Å—Sm(III) 0.96 Å). The conditions of the formation of each phosphate were investigated, and the colors of the crystals, the densities, and the infrared absorption spectra of various rare earth phosphates were also examined.

The chemistry of rare earth phosphates has developed rapidly in the last few years. Such rapid development may be attributed, first of all, to the use of neodymium ultraphosphate as a laser material.[1–4] Also, it may be attributed to the following circumstances. As for ultraphosphates, the existence of sodium[5,6] and calcium ultraphosphates[7,8] has been hitherto known, but they are unstable structures. However, stable rare earth ultraphosphates were reported by Jaulmes[9] in 1969 and by Bagieu-Beucher and Tranqui[10] in 1970, and their crystallographical interest has occasioned active studies of ultraphosphates.[11,12] Thus, the crystal structures of several rare earth ultraphosphates have been elucidated.[13] However, there have as yet been few systematic studies of rare earth phosphates, various problems regarding their chemical formulae, chemical names, species, methods of preparation, and physical properties remain unsolved. For instance ultraphosphate [$P_5O_{14}^{3-}$] is often called pentaphosphate,[14,15] but this name is unreasonable, for it invites confusion with non-branched chain pentaphosphate [$P_5O_{16}^{7-}$]. In phosphate chemistry, the term "ultraphosphate" is often used as a popular name of phosphates with a net-work structure; therefore, in the present paper [$P_5O_{14}^{3-}$] is designated "ultraphosphate." According to their definition, ultraphosphates, obviously differing from non-branched chain pentaphosphate, are phosphates with $P/Ln > 3$, where Ln=a trivalent rare earth metal, and have some branched P in their structures to form net-work structures.[5,7,16,17] On the other hand, the term "pentaphosphate" usually indicates non-branched chain phosphate [$P_5O_{16}^{7-}$] and not branched phosphate [$P_5O_{14}^{3-}$]. For neodymium *catena*-polyphosphate the chemical formula "NdP_3O_9" is often used,[11] but this formula properly indicates neodymium *cyclo*-triphosphate. Neodymium *catena*-polyphosphate is a long-chain polymer and should be indicated as $[Nd(PO_3)_3]_n$. However, because it is usually indicated as $Nd(PO_3)_3$, in the present study also $Nd(PO_3)_3$ will be used. However, it must be noted that NdP_3O_9 and $Nd(PO_3)_3$ obviously indicate several different compounds. Such being the case, there remain many obscurities regarding rare earth phosphates; moreover, no systematic studies of their preparation have been made at all. Further, it is considered that the establishment of preparation methods for various rare earth phosphates may contribute greatly to the development of the chemistry of rare earth phosphates. Thus, the present authors have investigated in detail the conditions of the formation of orthophosphates, pyrophosphate, *catena*-polyphosphates and ultraphosphates by the reactions of rare earth oxides with phosphoric acid; they have thus established the conditions of the formation of these phosphates.

Experimental

Preparation of Rare Earth Phosphates. In a gold or porcelain crucible, 99.9% portions of rare earth oxides (La_2O_3, CeO_2, Pr_6O_{11}, and Sm_2O_3 made by Shin-etsu Kagaku Co., Ltd.) was mixed with 85% orthophosphoric acid of a special grade in an atomic ratio P/Ln (R)=1—40, where Ln=La, Ce, Pr, and Sm; each mixture was dehydrated by heating with a weak flame. Each mixture gradually became viscous and gave a transparent liquid. However, in the region of R=1—3, an exothermic reaction occurred only by mixing each oxide with phosphoric acid, and the mixture solidified. Lanthanum oxide La_2O_3 reacted especially actively, while CeO_2 was inactive. Transparent liquids and matter obtained by the manner described above were heated in an electric furnace at 300—800 °C for 20 h to obtain rare earth phosphates (this is designated the thermal synthetic method). The color of each product obtained varied according to its metallic ion, its atomic ratio, its heating temperature, and its particle size. Rare earth phosphates prepared by the above method were generally hard, especially those prepared at high temperatures above 500 °C with R=1—5. Thus, these products were roughly crushed in a mortar, pulverized for about 30 min with a grinder, washed with distilled water, dried in a desiccator on silica gel, and then used for the following experiments.

Apparatus and Methods. *X-Ray Analysis*: X-Ray analysis was carried out with a Rigaku Denki Geigerflex X-ray diffractometer, using Ni-filtered Cu *Kα* radiation. The following conditions were used for the X-ray analysis: voltage 40 kV; current, 7 mA; counter range, 1000 c.p.s; time constant, 1 s, and scanning speed 1, 0.25, and 0.125°/min. The amounts of rare earth orthophosphate $LnPO_4 \cdot 0.5H_2O$ and $LnPO_4$, *catena*-polyphosphate $Ln(PO_3)_3$, ultraphosphate LnP_5O_{14}, cerium(IV) pyrophosphate CeP_2O_7 and *catena*-polyphosphate $Ce(IV)(PO_3)_4$ formed by the thermal synthetic method were determined from the integrated intensities of their characteristic X-ray diffraction peaks; *i.e.*, $LnPO_4 \cdot 0.5H_2O$ was determined by the peak at d=4.46 Å; $LnPO_4$, by that at 3.31 Å; $Ln(PO_3)_3$, by that at 3.43 Å; LnP_5O_{14}, by that at 3.72 Å; CeP_2O_7, by that at 4.33 Å, and $Ce(PO_3)_4$, by that at 4.04 Å.

Colorimetry. Colorimetry was carried out by the use of a color-difference meter (ND-101 type) made by the Nippon Denshoku Kogyo Co., Ltd. By using a halogen lamp as the light source, diffuse reflection light was collected with an integrating sphere and detected. In these experiments, the thickness of the sample layer in the measuring cell was always maintained above 10 mm, so that the reflectivity was not affected by the thickness of the layer. Also, the deviation of the reflectivity caused by the state of the sample layer was negligibly small. All experiments were carried out for samples with a particle size of 250—300 mesh.

Infrared Absorption Spectroscopy: A Hitachi EPI-S2 spectrophotometer was used for the infrared absorption spectroscopy, the spectra being taken by means of a KBr tablet or on Nujol mulls.

The densities of various rare earth phosphates were measured by means of a Beckmann air-comparison pycnometer.

Results and Discussion

Formation of Various Rare Earth Phosphates. In the La_2O_3, Pr_6O_{11}, and Sm_2O_3–H_3PO_4 systems four kinds of phosphates were formed; two kinds of orthophosphate $LnPO_4 \cdot 0.5H_2O$ (hexagonal) and $LnPO_4$ (monoclinic), *catena*-polyphosphate $Ln(PO_3)_3$, and ultraphosphate LnP_5O_{14}, while in the CeO_2–H_3PO_4 system, differing notably from the above systems, five kinds of phosphates —orthophosphate $CePO_4$, pyrophosphate CeP_2O_7, two types of *catena*-polyphosphate $Ce(III)(PO_3)_3$, and $Ce(IV)(PO_3)_4$, and ultraphosphate CeP_5O_{14}—were formed. The difference in the products of the CeO_2 system and those of the other systems may be caused by the fact that cerium can give stable phosphates of both Ce(III) and Ce(IV). On the contrary, lanthanum, praseodymium, neodymium, and samarium give only stable phosphates of La(III), Pr(III), Nd(III), and Sm(III), while no phosphates of Pr(IV) and Sm(II) were formed at all. Figure 1 shows some X-ray diffraction patterns of *catena*-polyphosphates. In this figure, the results for *catena*-polyphosphates of La, Pr, and Sm are shown as examples. However, for *catena*-polyphosphates of other metals (Ce(III) and Nd), X-ray diffraction patterns quite similar to those shown in Fig. 1 were also obtained. As can be seen from this figure, it is obvious that the series of *catena*-polyphosphates of all these rare earth metals are isomorphous, though slight deviations of diffraction peaks caused by the difference in the ionic radii of metals can be observed. That is, the X-ray diffraction peaks shifted toward smaller angles (larger d-values) with the increase in the ionic radii of rare earth metals. It was also proved that crystals of $LnPO_4 \cdot 0.5H_2O$ and $LnPO_4$ as well as crystals of LnP_5O_{14} were isomorphous.

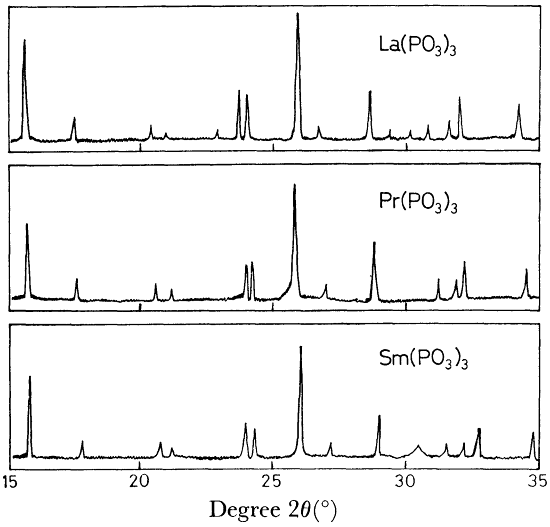

Fig. 1. X-Ray diffraction patterns of $Ln(PO_3)_3$. X-Ray used: Cu $K\alpha$(40 kV, 7 mA).

Relationship between Atomic Ratio P/Ln (R) and the Yields of Products. The reaction products of rare earth oxides with phosphoric acid seem to vary notably with the mixing ratio of the two components. The amounts of samarium ortho, *catena*-poly and ultraphosphates prepared in the Sm_2O_3-H_3PO_4 system at 700 °C for 20 h were determined from the integrated intensities of their characteristic X-ray diffraction peaks; the results are shown as a function of the mixing rate R=P/Sm in Fig. 2. As can be seen, at 700 °C three kinds of phosphates, $SmPO_4$, $Sm(PO_3)_3$, and SmP_5O_{14}, were formed. Orthophosphate $SmPO_4$ was formed in the R=1—2 range, while with R-values above 3 its formation was not observed at all. *catena*-Polyphosphate $Sm(PO_3)_3$ was formed in the range of R=2—8, in especially good yields in the R=3 range. This may be caused by the fact that P/Sm=3 just corresponds to the meta-composition. On the other hand, ultraphosphate began to form with R=4, and with R values above 10 was obtained in a pure form. Further, $SmPO_4 \cdot 0.5H_2O$ was formed with R= 1—2 at relatively low temperatures below 500 °C, while

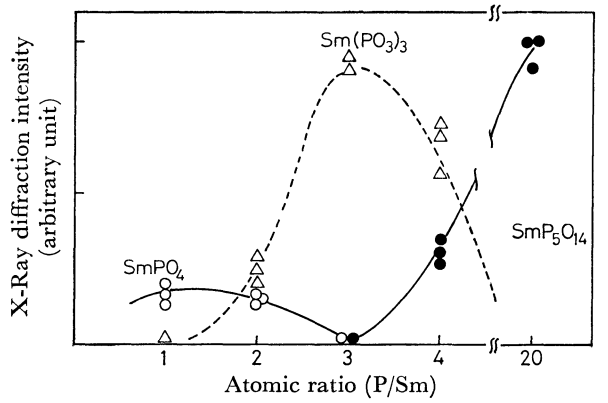

Fig. 2. Relationship between the yields of samarium phosphates and atomic ratio at 700 °C.

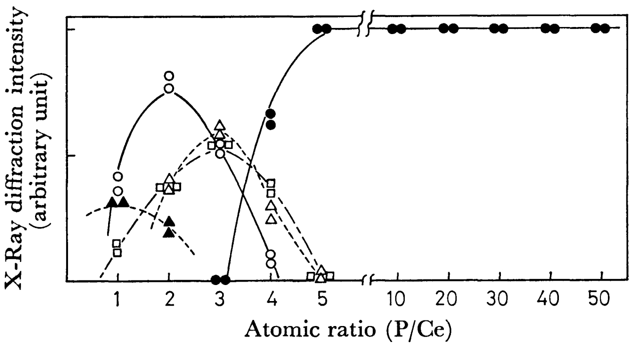

Fig. 3. Relationship between atomic ratio (P/Ce) and the yields of cerium phosphates at 800 °C. —▲—: $CePO_4$, —○—: CeP_2O_7, --□--; $Ce(PO_3)_3$, --△--: $Ce(PO_3)_4$, —●—: CeP_5O_{14}.

at temperatures above 600 °C its formation could not be observed at all. In the La_2O_3, Nd_2O_3, and Pr_6O_{11}–H_3PO_4 systems, almost the same tendency as that in the Sm_2O_3–H_3PO_4 system was observed. On the other hand, in the CeO_2–H_3PO_4 system a tendency markedly different from that in other systems was found, as is shown in Fig. 3, in which results obtained by heating a mixture of CeO_2 and H_3PO_4 at 800 °C for 20 h are shown. Orthophosphate $CePO_4$ was formed in the $R=$ 1—2 range, CeP_2O_7, in the $R=1$—4 range, $Ce(PO_3)_3$, in the $R=1$—4 range, and $Ce(PO_3)_4$, in the $R=2$—4 range. Thus, in the range of $R=1$—4 all these compounds were formed as mixtures, and it was impossible to obtain any of them in a pure form. On the other hand, CeP_5O_{14}, which was formed beginning at $R=4$, could be obtained purely at R above 5. Further, the present authors investigated the formation of cerium phosphates in the range of $R=50$—200 and at high temperatures (above 600 °C); only ultraphosphate was found to be obtained in all experiments. Also, no formation of $CePO_4 \cdot 0.5H_2O$ could be observed at all in the CeO_2–H_3PO_4 system.

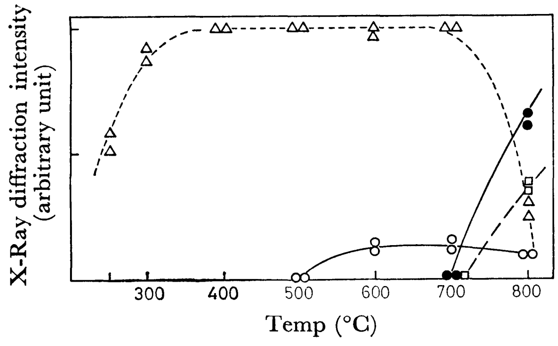

Fig. 4. Relationship between heating temperature and the yields of cerium phosphates in P/Ce=4. —○—: CeP_2O_7, --□--: $Ce(PO_3)_3$, --△--: $Ce(PO_3)_4$, —●—: CeP_5O_{14}.

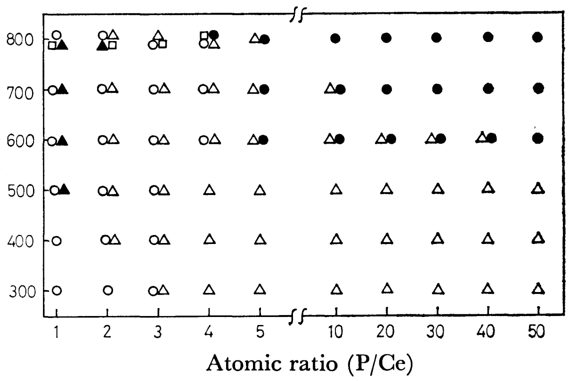

Fig. 5. Relationship of the species of cerium phosphates to heating temperature and atomic ratio. ▲: $CePO_4$, ○: CeP_2O_7, □: $Ce(PO_3)_3$, △: $Ce(PO_3)_4$, ●: CeP_5O_{14}.

Relationship between Heating Temperature and Products. The relation between the amounts of products and the heating temperature in the CeO_2–H_3PO_4 system with $R=4$ is shown in Fig. 4. As can be seen, cerium phosphates formed with $R=4$ were of four kinds: CeP_2O_7, $Ce(PO_3)_4$, $Ce(PO_3)_3$, and CeP_5O_{14}, and the formation of these compounds was strongly affected by the heating temperature. Pyrophosphate CeP_2O_7 was formed above 600 °C, but its yield was very small compared with those of the other products. This may be caused by the fact that the amount of phosphoric acid corresponding to $R=4$ is too much for the preparation of pyrophosphate, but lies in the ultra-component region. *catena*-Polyphosphate $Ce(PO_3)_4$ was formed in a wide temperature range (250—800 °C); especially, it could be obtained purely at 400—500 °C. At 600—700 °C, cerium *catena*-polyphosphate was contaminated with pyrophosphate. Further, at temperatures above 800 °C, the yield of $Ce(PO_3)_4$ decreased rapidly, and corresponding to its decrease, the formation of $Ce(PO_3)_3$ and CeP_5O_{14} was predominant. This phenomenon may be attributed to the transformation of Ce(IV) into Ce(III) through the decomposition of $Ce(PO_3)_4$, accompanied with oxygen evolution. Further studies of the decomposition mechanism and of the effects of the heating temperature and the heating atmosphere are now in progress. The relation between the heating temperature and the product in the R range from 1 to 50 is summarized in Fig. 5, in which the amount of each cerium phosphate obtained is wholly omitted. Cerium orthophosphate $CePO_4$ was formed with $R=1$ above 500 °C, while with $R=2$, it was formed at 800 °C. Pyrophosphate CeP_2O_7 was formed in the range $R=$ 1—3, regardless of the heating temperature, while with $R=4$, it was formed only at high temperatures (above 600 °C). On the other hand, the region of the formation of $Ce(PO_3)_4$ was wide as compared with those of the other cerium phosphates. It was proved that $Ce(PO_3)_4$ could be obtained in a pure form, especially at low temperatures below 500 °C with a large R, that is, in a much phosphoric acid region. However, with R-values of more than 20, because of the excess phosphoric acid a fairly long time (2—5 weeks) was necessary to form $Ce(PO_3)_4$ crystals; accordingly, the yield was decreased. It was also proved that $Ce(PO_3)_3$ was formed in the R range of 1—4 at high temperatures (above 800 °C) in the CeO_2–H_3PO_4 system; there existed no regions in which $Ce(PO_3)_3$ could be purely synthesized. Also, the formation of this compound could not be observed at all below 700 °C. On the other hand, CeP_5O_{14} was formed above 600 °C and $R \geqq 5$, in an especially large amount at 700—800 °C with R above 20. As has been reported previously, in the Nd_2O_3–H_3PO_4 system[18] the temperature of the formation of NdP_5O_{14} shifted toward the lower-temperature side with an increase in the P/Nd atomic ratio, that is, with an increase in the amount of phosphoric acid. For instance, with P/Nd= 4—5, the lower-temperature limit of NdP_5O_{14} formation was 500 °C, while with P/Nd above 10, the temperature of the formation has lowered to 400 °C. The temperature of the formation of CeP_5O_{14} in the CeO_2–H_3PO_4 system was quite high (above 600 °C), and no shift toward the lower-temperature side with an increase of R could be observed. This may be caused by the fact that only $Ce(PO_3)_4$ can exist stably at temperatures below 600 °C. It was also found that products in the CeO_2–H_3PO_4 system was notably different from those in the La_2O_3, Pr_6O_{11}, Nd_2O_3, and Sm_2O_3–H_3PO_4 systems. This difference may be explained as follows. In the CeO_2–H_3PO_4 system, both trivalent and quadrivalent cerium phosphates, that is, cerium(III) ortho, *catena*-poly, and ultraphosphates, as well as cerium(IV) pyro and *catena*-polyphosphates, can exist stably. On the other hand, all the phosphates of La, Pr, Nd, and Sm obtained in the present study were trivalent rare earth metal phosphates. The crystal structures (X-ray diffraction patterns and infrared absorption spectra) and properties (thermal change) of Ce(III) ortho, *catena*-poly, and ultraphosphates were

TABLE 1. PREPARATION OF RARE EARTH PHOSPHATES AT 300, 500, AND 700 °C

Ln	Temp °C	P/Ln 1	2	3	4	20	40
La	300	$LaPO_4\cdot0.5H_2O$(m) + $LaPO_4$(w)	$LaPO_4$(m) + $La(PO_3)_3$(w)	$LaPO_4$(w) + $La(PO_3)_3$(s)	$LaPO_4$(w) + $La(PO_3)_3$(s)	$La(PO_3)_3$(s)	$La(PO_3)_3$(s)
	500	$LaPO_4$(m)	$LaPO_4$(m) + $La(PO_3)_3$(m)	$La(PO_3)_3$(vs)	$La(PO_3)_3$(s) + LaP_5O_{14}(s)	LaP_5O_{14}(vs)	LaP_5O_{14}(vs)
	700	$LaPO_4$(m)	$LaPO_4$(m) + $La(PO_3)_3$(m)	$La(PO_3)_3$(vs)	$La(PO_3)_3$(s) + LaP_5O_{14}(s)	LaP_5O_{14}(vs)	LaP_5O_{14}(vs)
Ce	300	CeP_2O_7(m)	CeP_2O_7(vs)	CeP_2O_7(m) + $Ce(PO_3)_4$(w)	$Ce(PO_3)_4$(m)	$Ce(PO_3)_4$(s)	$Ce(PO_3)_4$(s)
	500	$CePO_4$(vw) + CeP_2O_7(m)	CeP_2O_7(vs) + $Ce(PO_3)_4$(w)	CeP_2O_7(s) + $Ce(PO_3)_4$(m)	$Ce(PO_3)_4$(vs)	$Ce(PO_3)_4$(vs)	$Ce(PO_3)_4$(vs)
	700	$CePO_4$(w) + CeP_2O_7(m)	CeP_2O_7(vs) + $Ce(PO_3)_4$(w)	CeP_2O_7(m) + $Ce(PO_3)_4$(m)	CeP_2O_7(vw) + $Ce(PO_3)_4$(vs)	CeP_5O_{14}(vs)	CeP_5O_{14}(vs)
Pr	300	$PrPO_4\cdot0.5H_2O$(w) + $PrPO_4$(w)	$PrPO_4$(m) + $Pr(PO_3)_3$(w)	$Pr(PO_3)_3$(s)	$Pr(PO_3)_3$(s)	$Pr(PO_3)_3$(vs)	$Pr(PO_3)_3$(vs)
	500	$PrPO_4$(m)	$PrPO_4$(m) + $Pr(PO_3)_3$(w)	$Pr(PO_3)_3$(s)	$Pr(PO_3)_3$(s) + PrP_5O_{14}(m)	PrP_5O_{14}(vs)	PrP_5O_{14}(vs)
	700	$PrPO_4$(m)	$PrPO_4$(m) + $Pr(PO_3)_3$(m)	$Pr(PO_3)_3$(s)	$Pr(PO_3)_3$(s) + PrP_5O_{14}(m)	PrP_5O_{14}(vs)	PrP_5O_{14}(vs)
Nd	300	$NdPO_4\cdot0.5H_2O$(m)	$NdPO_4$(m) + $Nd(PO_3)_3$(vw)	$NdPO_4$(m) + $Nd(PO_3)_3$(w)	$NdPO_4$(m) + $Nd(PO_3)_3$(m)	$Nd(PO_3)_3$(s)	$Nd(PO_3)_3$(vs)
	500	$NdPO_4$(m)	$NdPO_4$(w) + $Nd(PO_3)_3$(m)	$Nd(PO_3)_3$(s)	$Nd(PO_3)_3$(s) + NdP_5O_{14}(m)	NdP_5O_{14}(vs)	NdP_5O_{14}(vs)
	700	$NdPO_4$(m)	$NdPO_4$(m) + $Nd(PO_3)_3$(m)	$Nd(PO_3)_3$(vs)	$Nd(PO_3)_3$(s) + NdP_5O_{14}(m)	NdP_5O_{14}(vs)	NdP_5O_{14}(vs)
Sm	300	$SmPO_4\cdot0.5H_2O$(m)	$SmPO_4\cdot0.5H_2O$(m) + $SmPO_4$(w)	$SmPO_4$(m)	$SmPO_4$(m) + $Sm(PO_3)_3$(m)	$Sm(PO_3)_3$(s)	$Sm(PO_3)_3$(s)
	500	$SmPO_4\cdot0.5H_2O$(w) + $SmPO_4$(m)	$SmPO_4\cdot0.5H_2O$(w) + $SmPO_4$(m) + $Sm(PO_3)_3$(m)	$Sm(PO_3)_3$(s)	$Sm(PO_3)_3$(m) + SmP_5O_{14}(w)	SmP_5O_{14}(vs)	SmP_5O_{14}(vs)
	700	$SmPO_4$(m)	$SmPO_4$(m) + $Sm(PO_3)_3$(m)	$Sm(PO_3)_3$(s)	$Sm(PO_3)_3$(s) + SmP_5O_{14}(m)	SmP_5O_{14}(vs)	SmP_5O_{14}(vs)

X-Ray diffraction intensity: vs: very strong; s: strong; m: medium; w: weak; vw: very weak.

Table 2. Preparation of crystalline rare earth phosphates

	$LnPO_4\cdot 0.5H_2O$	$LnPO_4$	LnP_2O_7	$LnP_3O_9\cdot xH_2O$	$Ln_4(P_4O_{12})_3\cdot xH_2O$	$Ln(PO_3)_3$	$Ln(PO_3)_4$	LnP_5O_{14}
La(III) (1.061 Å)	I, II	I	—	II	II	I	—	I
Ce(III) (1.034 Å)	II	I	—	II	II	I	—	I
Ce(IV) (0.92 Å)	—	—	I	—	—	—	I	—
Pr(III) (1.013 Å)	I, II	I	—	II	II	I	—	I
Nd(III) (0.995 Å)	I, II	I	—	II	II	I	—	I
Sm(III) (0.964 Å)	I, II	I	—	II	II	I	—	I

I: Thermal synthetic method, II: aqueous solution reaction method, —: these phosphates can not be prepared by the methods of I and II.

similar to those of the corresponding phosphates of La, Pr, Nd, and Sm. In the lanthanum, cerium, praseodymium, neodymium, and samarium systems, experimental results on the preparation of the various rare earth phosphates described above are summarized in Table 1.

Results of studies of the formation of various crystalline phosphates prepared by the reactions of La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, or Sm_2O_3 with phosphoric acid (the thermal synthetic method), as well as those prepared by the reactions of aqueous solutions of $LaCl_3$, $CeCl_3$, $Ce(SO_4)_2$, $PrCl_3$, $NdCl_3$, or $SmCl_3$ with orthophosphoric acid or aqueous solutions of various sodium phosphates (this is designated as the aqueous solution reaction method) are summarized in Table 2. The compounds formed by the thermal synthetic method were $LnPO_4\cdot 0.5H_2O$, $LnPO_4$, $Ln(PO_3)_3$, and LnP_5O_{14} in the lanthanum, praseodymium, neodymium, and samarium systems, and $CePO_4$, CeP_2O_7, $Ce(PO_3)_3$, $Ce(PO_3)_4$, and CeP_5O_{14} in the cerium system. On the other hand, the crystalline compounds formed by the aqueous solution reaction method were $LnPO_4\cdot 0.5H_2O$, $LnP_3O_9\cdot xH_2O$, and $Ln_4(P_4O_{12})_3\cdot xH_2O$.

As La(III), Ce(III), Pr(III), Nd(III), and Sm(III) are almost equal in their ionic radii, they give isomorphic crystals of ortho, *cyclo*-tri, *cyclo*-tetra, *catena*-poly, and ultraphosphates. On the contrary, as crystalline phosphates of Ce(IV) only CeP_2O_7[19] and $Ce(PO_3)_4$[20] are known at present.

Colors of Rare Earth Phosphate Powders. Generally, the colors of rare earth phosphates prepared by the thermal synthetic method vary considerably depending on their preparation conditions (for example, the mixing rate of metallic oxides and phosphoric acid, or the heating temperature) and also on the sizes of their crystalline particles. However, the particle sizes were kept constant (250—300 mesh) in the present study, so the colors of the phosphates may depend strongly on the species of the products. In the lanthanum system, white crystals were obtained regardless of the atomic ratio and the heating temperature. In the cerium system, a light yellow cerium phosphate was obtained at low temperatures (below 500 °C), while above 500 °C with $R\geqq 10$ a white cerium phosphate was formed. In the neodymium system also, the colors of the crystals formed varied in the range from light blue to pink, according to the atomic ratio. In the praseodymium system, dark grey crystals were obtained with a small R, while with an increase in R, *i.e.*, with an increase in the amount of phosphoric acid, more yellowish green crystals were formed. In the samarium system, light yellow crystals were formed regardless of the atomic ratio and the heating temperature. The color changes

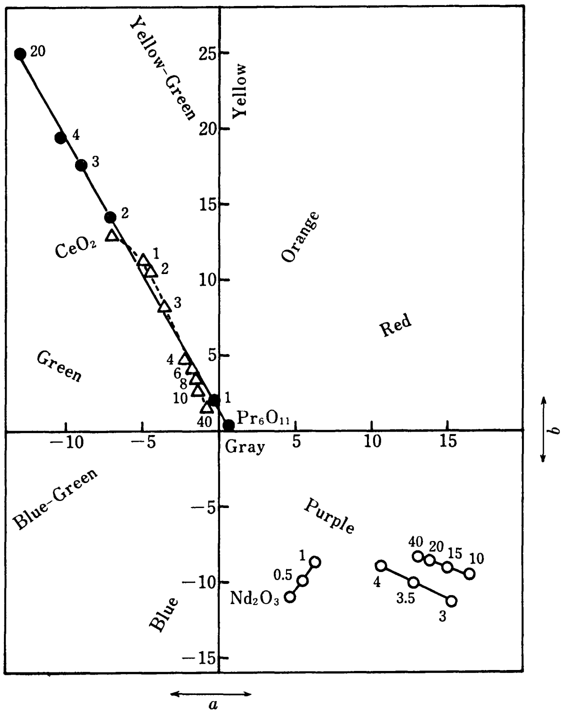

Fig. 6a. Changes of chromaticity coordinates (*a* and *b*) of cerium, praseodymium, and neodymium phosphates. --△--: Cerium, —●—: praseodymium, —○—: neodymium.

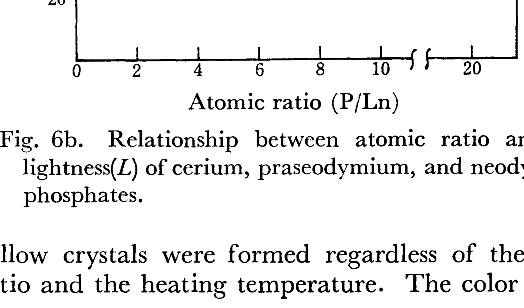

Fig. 6b. Relationship between atomic ratio and the lightness(L) of cerium, praseodymium, and neodymium phosphates.

of these rare earth phosphates will henceforth be expressed with the Lab system,[21,22] which is frequently used in colorimetry. The Lab system has perceptively almost uniform paces, and each color is expressed as a point in a three-dimensional color space. In the Lab system, L shows lightness and a, b show chromaticity coordinates, while a hue is expressed with $\theta=\tan^{-1} b/a$, and saturation, with $\sqrt{a^2+b^2}$. The Lab patterns of the phosphates obtained in the cerium, praseodymium, and neodymium systems are plotted against the atomic ratio in Figs. 6-a, b. The phosphates shown in Fig. 6 were prepared by heating at 700 °C for 20 h. In the cerium system, the product obtained at $R=0$—3 is light yellow, but with the increase in R it gradually becomes whitish. This is also supported by the results of colorimetry. It is found that the starting material (CeO_2) is light yellow, and with the increase in R (in other words, with the increase in the yields of CeP_2O_7, $Ce(PO_3)_4$, and CeP_5O_{14}), cerium phosphate approaches the hue of grey white, that is, to an achromatic color (saturation $\sqrt{a^2+b^2}=0$). However, the lightness, L, depends little on the atomic ratio, R.

In the praseodymium system, the color change is the reverse of that in the cerium system. That is, in the praseodymium system the color of the crystals changes from black (an achromatic color) to yellowish green. With R between 1 and 2, a and b change remarkably, while when R reaches 2, the product begins to turn yellowish green. This result corresponds to the increase in the yield of $Pr(PO_3)_3$, as is shown by the results of X-ray analysis. As the saturation increases with the increase in R, that is, with the successive formation of $PrPO_4 \rightarrow Pr(PO_3)_3 \rightarrow PrP_5O_{14}$, it is understandable that the product gains a brilliant hue. However, as $\theta=\tan^{-1} b/a$ is constant, no change in the hue of the product can be observed at all. On the other hand, as the lightness L varies rapidly in the R range of 0—2, the product obviously turns from black to white.

In the neodymium system, it is clearly observed that, with the increase in R, the color of the neodymium phosphates changes from blue through violet to pink; the results of colorimetry also show the existence of three different types of color changes. It is proved that the color of particles changes from blue to violet in the $R=0$—1 range, while in the $R=3$—4 range the product becomes more purple. However, in the R range from 3 to 4, as the saturation decreases it is apparent that the product approaches an achromatic color. Further, as the straight line on the a—b plane corresponding to $R=10$—40 shifts from that corresponding to $R=3$—4 toward the a-axis, the color of the product obviously changes from purple to red. While L is almost independent of R, the hues of the products with $R=0$—1, 3—4, and 10—40 are quite different from one another. This phenomenon suggests that, in the neodymium system, because of the wide variation in the color tones of the products from blue to red, the color of the particles is strongly affected by the species of neodymium phosphates formed; consequently, three different types of color changes are observed, as is shown in the figure.

Densities of Various Rare Earth Phosphates. The densities of the orthophosphates $LnPO_4$, *catena*-polyphosphates $Ln(PO_3)_3$, and ultraphosphates LnP_5O_{14} of La(III), Ce(III), Pr(III), Nd(III), and Sm(III), as well as of cerium(IV) *catena*-polyphosphate $Ce(PO_3)_4$, prepared by the thermal synthetic method are given in Table 3. The densities of rare earth orthophosphates, reported in detail by Mooney[23] and Weigel *et al.*,[24] are also given in the table for reference. For each metal, the density decreases in this order: $LnPO_4 \rightarrow Ln(PO_3)_3 \rightarrow LnP_5O_{14}$, showing that the P/Ln atomic ratio increases in the same order; the metallic ion content in unit cell of each crystal decreases accordingly.

Table 3. Densities of rare earth phosphates

	La	Ce	Pr	Nd	Sm
$LnPO_4$	5.18 5.09[23]	5.30[a] 5.23[23]	5.45 5.34[23]	5.53 5.50[23]	5.92 5.82[24]
$Ln(PO_3)_3$	3.46	3.57[a]	3.68	3.63	3.90
$Ce(PO_3)_4$		3.28			
LnP_5O_{14}	3.29	3.43	3.35	3.36	3.45

[a] Cerium orthophosphate, $CePO_4$, and *catena*-polyphosphate, $Ce(PO_3)_4$, were prepared by the reaction of $CeCl_3$ with H_3PO_4.

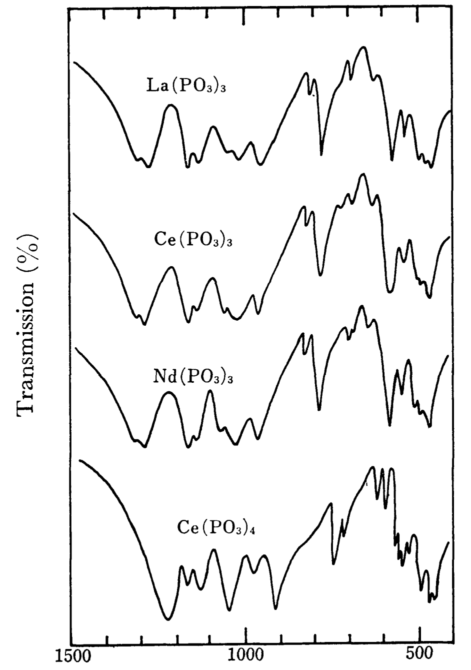

Fig. 7. IRS of $Ln(PO_3)_3$ and $Ce(PO_3)_4$.

Infrared Absorption Spectra (IRS). Figure 7 shows the IRS of $La(PO_3)_3$, $Ce(PO_3)_3$ (prepared by the reaction of $CeCl_3$ with H_3PO_4), $Nd(PO_3)_3$, and $Ce(PO_3)_4$, while Fig. 8 shows those of LaP_5O_{14}, CeP_5O_{14}, and NdP_5O_{14}. As can be seen from Figs. 7 and 8, the IRS of each phosphate is quite similar to those of the others; this fact strongly supports the above-presented conclusion of the X-ray diffraction study that each series of phosphates is crystallographically isomorphous. In the spectra of $Ln(PO_3)_3$, the absorption peaks at 1265—1300 cm^{-1} must be assigned to P=O; those at 1100—1200, 1000, and about 600 cm^{-1} to PO_3, and

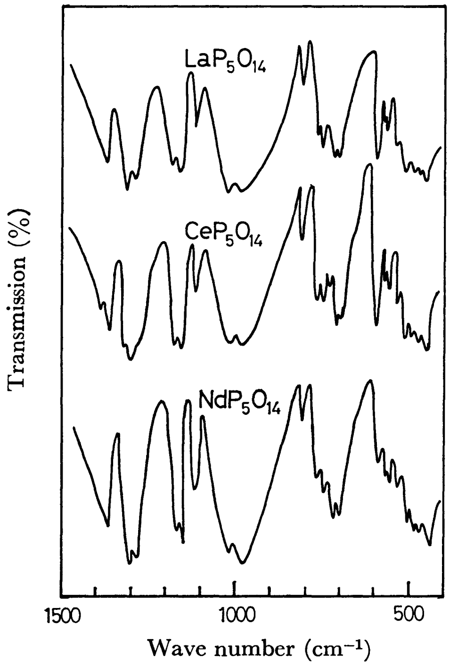

Fig. 8. IRS of LnP_5O_{14}.

those at 970 and about 830—750 cm^{-1}, to the P–O–P linkage. Further, the absorption spectrum of $Ce(PO_3)_4$ differs entirely from that of $Ce(PO_3)_3$, suggesting that the two compounds differ in bonding states from each other. However, for ultraphosphates the assignment of each absorption is not yet clear.

Conclusion

The experimental results can be summarized as follows:

1) In the La_2O_3, Pr_6O_{11}, and Sm_2O_3-H_3PO_4 systems, orthophosphate, *catena*-polyphosphate, and ultraphosphate are obtained.

2) In the CeO_2-H_3PO_4 system, trivalent and quadrivalent cerium phosphates, *i.e.*, cerium(III) ortho, *catena*-poly, and ultraphosphates, as well as cerium(IV) pyro and *catena*-polyphosphates can be prepared. The main products in this system are CeP_2O_7, $Ce(PO_3)_4$, and CeP_5O_{14}.

3) The crystal of each corresponding phosphate (ortho, *catena*-poly, and ultraphosphates) of La, Ce(III), Pr, Nd, and Sm is isomorphous.

4) In the lanthanum, praseodymium, and samarium systems, $LnPO_4 \cdot 0.5H_2O$ is readily formed at 300 °C with an atomic ratio of $R=1$, while $LnPO_4$ is formed at high temperatures (above 600 °C) with $R=1$. *catena*-Polyphosphate $Ln(PO_3)_3$ can be prepared above 500 °C with $R=3$ or by heating at 300 °C for 2—7 d with $R \geqq 10$. Ultraphosphate LnP_5O_{14} is obtained by heating at temperatures above 500 °C with $R \geqq 10$.

5) Cerium pyrophosphate CeP_2O_7 is formed with $R=1$—3, regardless of the heating temperature, while $Ce(PO_3)_4$ is easily obtained at low temperatures (below 500 °C) over a larger R region. Ultraphosphate CeP_5O_{14} can be synthesized purely at 700—800 °C with $R \geqq 20$.

6) Lanthanum phosphates are white, while cerium(IV) and cerium(III) phosphates are yellow and white respectively. Praseodymium phosphates are green, neodymium phosphates with a small R are bluish violet, those with a larger R are pink, and samarium phosphates are light yellow.

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