Solid State Reactions between Rare Earth Orthophosphate and Oxide

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Synopsis. Solid state reactions between rare earth orthophosphate (RPO_4) and oxides (SiO_2, Al_2O_3, or CaO) in the air were studied by means of X-ray diffractometry. RPO_4 does not react with SiO_2, decomposing on heating above 1800 °C with Al_2O_3, or above 700 °C with CaO.

Anhydrous RPO_4 is stable in the air at temperatures near 2000 °C.[1,2] However, no study seems to have been carried out on the solid state reactions of RPO_4 with other oxides. The present study deals with such reactions between synthesized RPO_4 (R=La, Ce, Nd, Sm, Y, Dy, Er, or Yb) and oxides (SiO_2, Al_2O_3, or CaO) at temperatures in the range 600—1900 °C in the air.

Experimental

Starting Materials. Powder of monoclinic RPO_4 (R=La, Ce, Nd, or Sm) and that of tetragonal RPO_4 (R=Y, Dy, Er, or Yb), particle size less than 1 μm, and chemical composition very similar to that of theoretical RPO_4, were prepared by the methods reported[1,3-5]. Powder of SiO_2 (α-quartz, Wako Chemical Ind., Ltd.), Al_2O_3 (α-alumina, Nishio Ind., Ltd.) and CaO (Nakarai Chemicals, Ltd.), of high purity and less than 62 μm in length, were prepared from substances of reagent grade.

Solid State Reactions. Mixtures of RPO_4 and oxide in mole ratio 0.1—1 (RPO_4/oxide) were pressed at room temperature into pellets, *ca.* 10 mm diam. under the pressure 500 kgf/cm² (1 kgf/cm²=98.0665 kPa). The pellets were preheated at 600 °C, and then calcined in the temperature range 600—1900 °C for 60 min in an alumina crucible by using a SiC electric furnace (600—1500 °C) or an oxygen-propane gas furnace (1500—1900 °C).

Results and Discussion

Reaction with SiO_2. RPO_4 did not react with SiO_2 at temperature below 1700 °C. X-Ray diffraction patterns of the pellets calcined in the temperature range 600—1700 °C showed only the diffraction lines of the starting materials and none of new reaction products. The pellets softened with an increase in the amount of SiO_2 above 1713 °C (melting point of SiO_2) in the air.

Reaction with Al_2O_3. When the pellets were calcined below 1750 °C, X-ray diffraction patterns were those of the starting materials. However, some pellets (R=Nd, Sm, Y, Dy, Er, or Yb) calcined at 1800 °C and others (R=La, or Ce) calcined at 1850 °C for 60 min showed X-ray diffraction patterns of the reaction products (R_2O_3 or CeO_2).

The X-ray peak intensity of Al_2O_3 in the calcined pellets seems to be little affected by the calcining temperature and the decomposition of RPO_4, while that of R_2O_3 or CeO_2 was much affected, becoming strong with the decomposition of RPO_4. At 1900 °C, the X-ray diffraction lines of RPO_4 disappeared, only Al_2O_3 and R_2O_3 or CeO_2 becoming the main constituents of the calcined pellets. The amount of P of the calcined pellets determined by chemical analysis decreased gradually with the progress of the decomposition of RPO_4 above 1800 °C.

$AlPO_4$ is easily formed by heating mixtures of Al_2O_3 and P_2O_5 in the air. However, no $AlPO_4$ was detected in the pellets calcined at temperatures above 1800 °C for 60 min. Beck[6] reported that $AlPO_4$ is easily decomposed within a few minutes by heating at temperature above 1590 °C in the air, P component evaporating rapidly. Thus, even if $AlPO_4$ is formed in the pellets at temperatures above 1800 °C, it would be decomposed within a few minutes, its detection becoming difficult.

The reaction process might be expressed as follows:

$$2RPO_4 + Al_2O_3 \longrightarrow 2AlPO_4 + R_2O_3 \longrightarrow Al_2O_3 + R_2O_3 + (\text{P component}\uparrow)$$

$$\text{or}\quad 2CePO_4 + Al_2O_3 + 1/2O_2 \longrightarrow 2AlPO_4 + 2CeO_2 \longrightarrow Al_2O_3 + 2CeO_2 + (\text{P component}\uparrow) \quad (1)$$

$$2RPO_4 \xrightarrow{Al_2O_3} R_2O_3 + (\text{P component}\uparrow), \text{ or}$$

$$2CePO_4 \xrightarrow[1/2O_2]{Al_2O_3} 2CeO_2 + (\text{P component}\uparrow) \quad (2)$$

The process is based on the following assumptions: in (1) $AlPO_4$ can be formed in the calcined pellets in the early stages of reaction, and in (2) Al_2O_3 catalyzes the decomposition of RPO_4 in the calcined pellets, and no $AlPO_4$ can be formed because of high temperature.

It is apparent that RPO_4 can be decomposed by Al_2O_3 above 1800 °C in the air. However, which process takes place has not been clarified.

The melting points of Al_2O_3 and R_2O_3 or CeO_2 are higher than 1900 °C. However, the pellets softened at *ca.* 1900 °C, a part of the alumina crucible in contact with the pellets undergoing corrosion. The reason for the pellets softening at *ca.* 1900 °C can be explained by means of the phase diagrams of the systems Al_2O_3–R_2O_3 or CeO_2.[7] There are eutectic points such as 1720 °C (Al_2O_3 77 mol%+Nd_2O_3 23 mol%) or 1850 °C (Al_2O_3 20 mol%+Nd_2O_3 80 mol%) in the Al_2O_3–Nd_2O_3 system.

Reaction with CaO. RPO_4 reacted with CaO at temperatures above 700 °C, $Ca_3(PO_4)_2$ and R_2O_3 or CeO_2 being formed as new reaction products. The ratios of the decomposition of RPO_4 at temperature above 700 °C are expressed by means of the relative X-ray peak intensity ($I_1/(I_1+I_2)$) as shown in Fig. 1.

l_1 is the X-ray integrated peak intensity of RPO_4 ((200) diffraction line), and l_2 that of R_2O_3 or CeO_2 (diffraction line having the strongest intensity in the d range 2.95 (La_2O_3)—3.12 Å (CeO_2)(1 Å=0.1 nm).

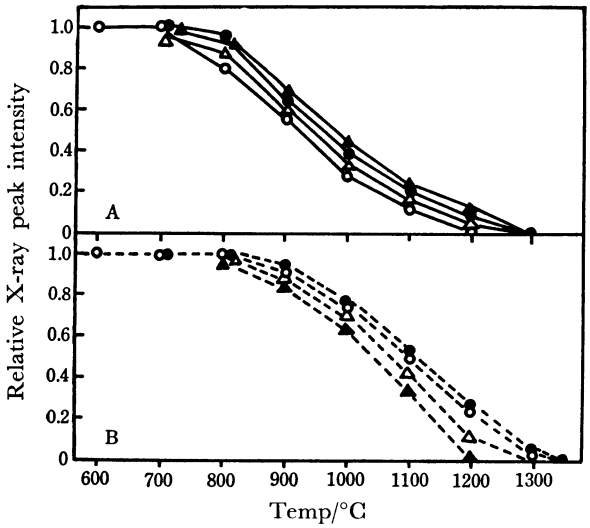

Fig. 1. Relation between the relative X-ray peak intensity and the firing temperature of the pellets[a] fired at various temperatures (600—1350 °C) for 60 min.

a) Mixing mole ratio (RPO_4/CaO) 0.6, A: Monoclinic form RPO_4, B: Tetragonal form RPO_4, ○—○: R=La, ●—●: R=Ce, △—△: R=Nd, ▲—▲: R=Sm, ○---○: R=Y, ●---●: R=Dy, △---△: R=Er, ▲---▲: R=Yb.

The relative X-ray peak intensity began to decrease at 700 °C, becoming O at 1350 °C (mixing mole ratio (RPO_4/CaO) below 0.6). The rate of decomposition of monoclinic RPO_4(A) seems to be slightly higher than that of tetragonal RPO_4(B) (Fig. 1).

The reaction products detected in the calcined pellets were only $Ca_3(PO_4)_2$ and R_2O_3 or CeO_2. The reaction process could be expressed by

$$2RPO_4 + 3CaO \longrightarrow Ca_3(PO_4)_2 + R_2O_3$$

$$\text{or } 2CePO_4 + 3CaO + 1/2O_2 \longrightarrow Ca_3(PO_4)_2 + 2CeO_2 \quad (3)$$

The pellets softened at temperature below 1800 °C in the air since the melting point of $Ca_3(PO_4)_2$ is lower than that of RPO_4.

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