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Syntheses of Rare Earth Orthophosphates

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Synopsis. Rare Earth orthophosphates have been synthesized and examined by X-ray diffraction, DTA and TGA. Six types have been found: a) the monazite type RPO_4, b) the xenotime type RPO_4, c) the hexagonal form $RPO_4 \cdot 0.5H_2O$, d) the weinschenkite type $RPO_4 \cdot 2H_2O$, e) the orthorhombic form $DyPO_4 \cdot 1.5H_2O$ and f) the amorphous phosphate.

In preceding papers,[1-4] the synthesized monazite type $CePO_4$, the hexagonal form $CePO_4 \cdot 0.5H_2O$, the xenotime type YPO_4, and the weinschenkite type $YPO_4 \cdot 2H_2O$ have been reported. The present study reports the syntheses and thermal stability of various rare earth orthophosphates RPO_4 (R=La, Ce, Pr, Nd, Sm, Gd, Y, Dy, Er, or Yb).

Experimental

Starting Materials. RCl_3 of 99.9% purity (R=La, Ce, Pr, Nd, Sm, Gd, Y, Dy, Er, or Yb) and H_3PO_4, $(NH_4)H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_3PO_4 \cdot 3H_2O$ or $NaPO_3$ were used as starting materials.

Synthesis by Solid State Reactions. Mixtures of RCl_3 and $NaPO_3$ with a mole ratio (P/R) of 2.5 were heated in the temperature range 200—1000 °C for 5 h in an electric furnace using a platinum crucible. After heating, the hot crucible was removed from the furnance and quenched to room temperature. The products were taken out from the crucible and washed successively with $(1+10)HNO_3$ solution, distilled water and acetone.

Synthesis by Precipitation. A solution of RCl_3 (0.05 mol/l) was rapidly added to dilute H_3PO_4 or phosphate solution and magnetically stirred. After one hour, the pH of the mixed solution was measured by a pH meter and the solution transfered to a conical flask, which was tightly stoppered. The mixed solutions were maintained at 20, 50, and 90 °C for 1 to 900 days in an air bath. The pH of the mixed solution was adjusted to a constant value with H_3PO_4 or phosphate solution. The solution was suction-filtered with a filter paper and washed five times with distilled water and finally with acetone. The precipitate was kept in a desiccator (drying agent: H_2SO_4) at room temperature.

Results and Discussion

Phases Obtained by Solid State Reaction. Feigelson[5] synthesized anhydrous RPO_4 by the fusion of rare earth oxides with excess $Pb_2P_2O_7$ at 1300 °C in a refractory (mullite) crucible in an electric furnace.

In the present investigation, the anhydrous phosphates of monazite type RPO_4 (R=La, Ce, Pr, Nd, Sm, or Gd) and xenotime type RPO_4 (R=Y, Dy, Er, or Yb) were first synthesized by the solid state reactions in air of RCl_3 with $NaPO_3$ at temperatures as low as 200 °C. No hydrated phosphates were detected in the heated samples. The intensity of the X-ray diffraction powder lines of the anhydrous phosphates increased with increasing preparation temperature.

Phases Obtained by Precipitation. Anthony[6] synthesized the monazite type $CePO_4$ by the hydrothermal treatment of mixtures of cerium hydroxide gel, H_3PO_4 and water at *ca.* 300 °C. Hydrated phosphates were not observed in the products.

In the present investigation, various types of phosphates were synthesized below 90 °C in solution. The crystalline phases obtained by precipitation from mixed solutions in the temperature range 20—90 °C for 1 to 900 days were the hexagonal form $RPO_4 \cdot 0.5H_2O$ (R=La, Ce, Pr, Nd, Sm, or Gd), the weinschenkite type $RPO_4 \cdot 2H_2O$ (R=Y, Dy, Er, or Yb), the orthorhombic form $DyPO_4 \cdot 1.5H_2O$, the monazite type RPO_4 (R=La, Ce, Pr, Nd, Sm, or Gd) and the xenotime type RPO_4 (R=Y, Dy, Er, or Yb). Table 1 illustrates the phases obtained by X-ray diffraction analysis under various experimental conditions.

The hexagonal form $RPO_4 \cdot 0.5H_2O$ was synthesized in the pH range 1—3 at 20 °C and was stable in the mother liquor for 900 days. Above 50 °C, however, the hexagonal form gradually changed into the monazite type RPO_4 in the solution. The rate of transformation from the hexagonal form to the monazite type by ageing in solution increased with decreasing pH and increasing preparation temperature. The weinschenkite type $RPO_4 \cdot 2H_2O$ was synthesized in the pH range 1—3 at 20 °C and was stable in solution for 900 days. When aged above 50 °C the weinschenkite type gradually changed to the xenotime type RPO_4. Amorphous phosphate was detected in the precipitate from the mixed solution above pH 3 at 20 °C. After ageing in solution above 50 °C, the amorphous phosphate became the crystalline hydrated or anhydrous phosphates of the hexagonal form, weinschenkite type, orthorhombic form, monazite type or xenotime type, depending on the kind of rare earth.

Thermal Stability. It has been established that monazite and xenotime are stable in air at high temperatures. Ueda and Korekawa,[7] and Ueda[8] found that the cone of natural monazite from Nogisawa-mura, Fukushima Pref. did not melt when fired at 1950 °C, and that natural xenotime from Ishikawa-cho, Fukushima Pref. did not decompose at 1800 °C. The thermal stability of the hydrated rare earth orthophosphates has been reported only for $CePO_4 \cdot 0.5H_2O$[9] and $YPO_4 \cdot 2H_2O$.[3]

The DTA curves of the hexagonal form $RPO_4 \cdot 0.5H_2O$ showed two endothermic peaks and the TGA curves showed a weight loss corresponding to $0.5H_2O$ at 204—234 °C. This weight loss appeares to correspond to the first endothermic DTA peak (204—234 °C).

Table 1. Synthetic runs and phases detected

R	Aging time (day)	Detected phases											
		20 °C (pH)				50 °C (pH)				90 °C (pH)			
		0.5	1	3	5	0.5	1	3	5	0.5	1	3	5
La	3	—	H	H	A	—	H	H	A	M+H	H	H	A
	14	—	H	H	A	M+H	H	H	A	M+H	H	H	A
	28	—	H	H	A	M+H	H	H	A	M	H	H	A
	900	—	H	H	A	M	M	M	M	M	M	M	M
Gd	3	—	H	H	A	—	H	H	A	M+H	H	H	H
	14	—	H	H	A	H	H	H	H	M+H	H	H	H
	28	—	H	H	A	M+H	H	H	H	M	H	H	H
	900	—	H	H	A	M	M	M	M	M	M	M	M
Dy	3	—	W	A	A	—	W	O	A	—	O	O	O
	14	—	W	W	A	—	W	O	A	O	O	O	O
	28	—	W	W	A	W	W	O	A	O	O	O	O
	900	—	W	W	A	X	X	X	X	X	X	X	X
Y	3	—	W	A	A	—	W	W	A	—	W	W+X	X
	14	—	W	W	A	—	W	W	A	X	X	X	X
	28	—	W	W	A	—	W	W	X	X	X	X	X
	900	—	W	W	A	—	X	X	X	X	X	X	X
Yb	3	—	W	A	A	—	W	A	A	X	X	X	A
	14	—	W	W	A	X+W	X+W	X	A	X	X	X	X
	28	—	W	W	A	X	X	X	A	X	X	X	X
	900	—	W	W	A	X	X	X	X	X	X	X	X

—: No precipitate, H: hexagonal form $RPO_4 \cdot 0.5\ H_2O$, M: monazite type RPO_4, W: weinschenkite type $RPO_4 \cdot 2H_2O$, A: amorphous phosphate, X: xenotime type RPO_4, O: orthorhombic $DyPO_4 \cdot 1.5H_2O$.

Dehydrated RPO_4 had a hexagonal form and was easily rehydrated to form $RPO_4 \cdot 0.5H_2O$ when kept at ordinary humidity. Therefore this water corresponding to $0.5H_2O$ was concluded to be zeolitic water. The anhydrous hexagonal form RPO_4 gradually transformed into the monazite type at 500—600 °C. The DTA curves of the synthesized weinschenkite type $RPO_4 \cdot 2H_2O$ showed one endothermic peak and the TGA curves showed a weight loss corresponding to $2H_2O$ at 273—276 °C. This weight loss appeares to correspond to the endothermic DTA peak (273—276 °C). Anhydrous RPO_4 was xenotime type. The weinschenkite type $RPO_4 \cdot 2H_2O$ appeared to convert to the xenotime type in air in the temperature range 273—276 °C. The orthorhombic form $DyPO_4 \cdot 1.5H_2O$ converted to the xenotime type $DyPO_4$ at 270 °C in air.

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