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Phase Equilibria in the System $CePO_4$–Na_3PO_4

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The phase diagram of the system $CePO_4$–Na_3PO_4 has been determined by differential thermal, X-ray, and microscopic methods. The system contains only one intermediate compound, $Na_3Ce(PO_4)_2$, which melts incongruently at 1550°C. This compound is stable down to room temperature and exhibits a polymorphic transition at 1060°C. The low-temperature modification has an orthorhombic (lattice type *P*) unit cell with parameters $a = 14.074(1)$, $b = 16.039(1)$, and $c = 18.607(1)$ Å; $V = 4200.21$ Å^3.

Introduction

Investigations of sodium–cerium (III) phosphates have been carried out in our laboratory for several years. Continuing previous work (*1, 2*), we present the current results of a study of the system $CePO_4$–Na_3PO_4. The phase diagram of this system has not been published until now, but some information is available about the intermediate compounds.

As can be concluded from the literature reports, two types of double orthophosphates, $M^I_3M^{III}(PO_4)_2$ and $M^I_3M^{III}_2(PO_4)_3$ (where M^I = alkali metals; M^{III} = lanthanides, Sc, Y), are known. These compounds, according to their composition, occur in the systems $M^{III}PO_4$–$M^I_3PO_4$.

There are many papers including the methods of synthesis, the results of X-ray examinations, and possibilities of application of these compounds. Bamberger *et al.* (*3*) reported an extensive literature review of synthesis and characterization of phosphates containing alkali metals and lanthanides.

In 1977, Kizilyalli and Welch (*4*) prepared compounds of the type $M^I_3M^{III}(PO_4)_2$ (where M^I = Na; M^{III} = La, Ce, Nd, Gd, and Y) by means of several different reactions. According to these authors, $M^I_3M^{III}(PO_4)_2$ compounds (α or "low" temperature form) crystallized in the tetragonal system. According to Salmon *et al.* (*5*), these compounds should crystallize in the orthorhombic system.

In 1979, Bamberger *et al.* (*6*) described a new preparative method and characterization of double phosphates containing cerium (III) and alkali metals: $M^I_3Ce(PO_4)_2$. The authors studied the reactions of CeO_2 with various alkali metal hydrogen orthophosphates, metaphosphates, and pyrophosphates at temperatures up to 1000°C. The analysis of solid phase products of these reactions by powder X-ray diffraction indicated the formation of $Na_3Ce(PO_4)_2$ and $K_3Ce(PO_4)_2$. The authors also prepared

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these phosphates by firing mixtures of Na_3PO_4 (or K_3PO_4) with $CePO_4$ at 500°C in air, followed by a further firing at 950°C in flowing helium. According to Ref. (*6*), the mixed phosphates are nearly white, but change (reversibly) to yellow-orange when heated. Infrared spectra of $Na_3Ce(PO_4)_2$ show broad bands at 990–1300 cm^{-1} and at 530–660 cm^{-1}.

Experimental

The following original analytical-reagent-grade substances were used: $Ce(NO_3)_3 \cdot 6H_2O$, $NH_4H_2PO_4$, and $Na_3PO_4 \cdot 12H_2O$.

Samples in the system $CePO_4$–Na_3PO_4 were prepared from the initial orthophosphates. Cerium (III) orthophosphate was prepared by the method provided in (*6*). Sodium orthophosphate Na_3PO_4 was obtained by slow dehydration of $Na_3PO_4 \cdot 12H_2O$ at 200, 300, and further at 600°C. The samples were synthesized preliminarily at 1150°C each time.

The phase investigations were carried out by differential thermal analysis (cooling and heating), by powder X-ray diffraction, by microscopy in reflected light, and IR-absorption. The differential thermal analysis of heating was performed by means of a derivatograph type 3427 (MOM, Hungary), heating rate 10°/min, platinum cup, and air atmosphere. The standard substance used was high-purity Al_2O_3. The differential thermal analysis of cooling was performed in a furnace constructed in our laboratory, under air. Temperatures were measured by means of a Pt/Pt 10 Rh thermocouple, which was calibrated against the melting points of $Ca_2P_2O_7$, K_2SO_4, and the polymorphic transition point of K_2SO_4 (583°C). Temperatures above 1400°C were read by means of an optical pyrometer, which was calibrated against the melting points of Na_3PO_4 and $Ca_3(PO_4)_2$.

A quenching technique was also used for phase determination. The phases were identified by powder X-ray diffraction. An HZG-4 diffractometer with Cu$K\alpha$ radiation was used.

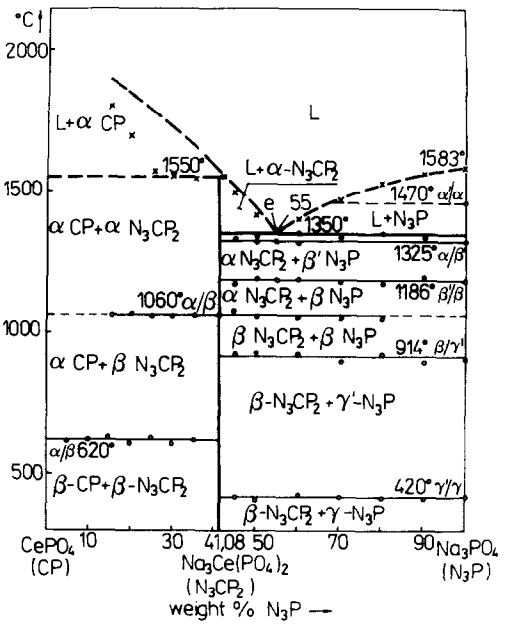

FIG. 1. Phase diagram of the system $CePO_4$–Na_3PO_4: ●, thermal analysis (heating); x, optical.

The phase structure of the products was also controlled microscopically in reflected light.

The Specord IR-75 spectrophotometer was used for the IR absorption spectroscopy using pellets formed by mixing the specimens with KBr.

Results and Discussion

The phase diagram of system $CePO_4$–Na_3PO_4 is presented in Fig. 1.

Examinations of polymorphic modifications of initial orthophosphates proved that $CePO_4$ occurs in two polymorphic modifications, and the temperature of transition is 620°C (according to (*7*) it is 700°C). According to literature data, sodium orthophosphate Na_3PO_4 shows many polymor-

TABLE I

X-RAY ANALYSIS DATA FOR β-$Na_3Ce(PO_4)_2$ MODIFICATION

hkl	d_{obs}(Å)	d_{calc}(Å)	Intensities
111	9.25	9.20	
002		9.29	2
201	6.59	6.58	32
032	4.65	4.64	
203		4.65	56
004		4.65	
132	4.42	4.41	
104		4.41	<1
231	4.15	4.15	15
040	4.01	4.02	<1
232	3.873	3.873	
204		3.876	1
124		3.867	
233	3.511	3.510	
400		3.516	14
034		3.509	
411	3.373	3.377	
043		3.370	<1
025		3.373	
402	3.292	3.288	
332		3.298	2
420	3.222	3.221	
412		3.222	2
215		3.219	
403	3.059	3.058	2
052	3.034	3.037	
243		3.039	
044		3.038	3
106		3.025	
432	2.802	2.802	
404		2.804	100
235		2.801	
036	2.682	2.681	
145		2.679	47
226	2.673	2.673	
060		2.677	38
520	2.658	2.655	
512		2.655	5
433		2.655	
253	2.641	2.643	
054		2.643	1
261	2.476	2.480	
254		2.474	4
601	2.328	2.326	
360		2.325	6
336		2.327	
362	2.254	2.256	
237		2.253	4

TABLE I—*Continued*

hkl	d_{obs}(Å)	d_{calc}(Å)	Intensities
172	2.203	2.201	
264		2.203	
156		2.202	1
208		2.206	
128		2.204	
631	2.132	2.133	
460		2.130	
436		2.132	16
038		2.131	
623	2.113	2.115	
454		2.113	3
247		2.112	
614	2.074	2.075	
462		2.076	2
265		2.076	
623	2.029	2.029	
624		2.025	
066		2.026	2
157		2.025	
119		2.026	
641	2.013	2.013	
463		2.015	
372		2.013	
446		2.012	2
356		2.014	
328		2.015	
182	1.945	1.944	
266		1.946	<1
721	1.940	1.938	
560		1.939	
536		1.941	11
408		1.938	
338		1.940	
464	1.936	1.936	
175		1.934	22
248		1.933	
730	1.882	1.881	
472		1.882	
456		1.883	3
275		1.882	
058		1.883	
800	1.760	1.758	7
661	1.755	1.756	
654		1.754	
092		1.753	
466		1.755	4
185		1.753	
068		1.755	
2210		1.753	

Continued

TABLE I—*Continued*

hkl	d_{obs}(Å)	d_{calc}(Å)	Intensities
0310		1.756	
830	1.668	1.670	
390		1.668	
293		1.667	
637		1.670	2
094		1.666	
1111		1.668	
831	1.664	1.664	
391		1.662	2
509		1.664	
832	1.645	1.644	
804		1.644	
566		1.644	11
368		1.643	
3310		1.644	
665	1.594	1.593	
717		1.594	<1
269		1.592	
834	1.573	1.572	
1102		1.573	7
492	1.568	1.569	
2100		1.566	
295		1.569	6
2510		1.568	

Note. Orthorhombic system: a = 14.074(1), b = 16.039(1), and c = 18.607(1) Å; V = 4200.21 Å.

phic transitions. During our experiments, we found the existence of only four of them, namely: α/β', 1325°C; β'/β, 1186°C; β/γ', 914°C; and γ'/γ, 420°C.

It was discovered that $CePO_4$ and Na_3PO_4 reacting at the 1 : 1 molar ratio form a compound with the formula $Na_3Ce(PO_4)_2$. It melts peritectically at approx. 1550°C and is stable down to room temperature. The peritectic reaction finishes at the composition 42.0 wt% of Na_3PO_4. In the system $CePO_4$–Na_3PO_4, a eutectic occurs at the composition 55 wt% of Na_3PO_4, at 1350°C.

Thermal investigations showed that the compound $Na_3Ce(PO_4)_2$ has a polymorphic transition which occurs at different temperatures according to the thermal treatment which is used. During the thermal analysis on heating of the previously melted $Na_3Ce(PO_4)_2$, two effects occur on the DTA curves, at 920 and 1040°C. The thermal effect at 1040°C is strong. During the thermal analysis on cooling, one strong thermal effect at 1060°C occurs on the DTA curves. $Na_3Ce(PO_4)_2$ samples presynthesized by sintering at 1150°C behave in a different way. During the thermal analysis on heating, one strong effect occurs at 1060°C on the DTA curves, while during the cooling two effects appear at 1060 and 920°C. The effect at 1060°C is strong.

Transition α/β – $Na_3Ce(PO_4)_2$ in the system $CePO_4$–Na_3PO_4, forms analogical thermal effects as $Na_3Ce(PO_4)_2$ pure. It brings us to a conclusion that the polymorphic transition of $Na_3Ce(PO_4)_2$ can proceed either in a temperature interval, or at one definite temperature. The high-temperature modification, α – $Na_3Ce(PO_4)_2$, cannot be stabilized at room temperature by quenching in air or ice. The low-temperature modification, β – $Na_3Ce(PO_4)_2$, was investigated with X-ray diffraction. The applied X-ray techniques, including both the experimental conditions, the equipment that had been used, and the numerical interpretation of the data, were those described in (*8*).

It was found that the low-temperature modification, β – $Na_3Ce(PO_4)_2$, has an orthorhombic structure (lattice type P), and cell parameters a = 14.074(1), b = 16.039(1), and c = 18.607(1) Å; V = 4200.21 Å^3. Table I presents the powder X-ray diffraction data of β – $Na_3Ce(PO_4)_2$.

In the binary system $CePO_4$–Na_3PO_4, within the composition range 0–40 wt% of Na_3PO_4, a thermal effect occurs at approx. 620°C. It results from the α/β – $CePO_4$ polymorphic transition. The polymorphic transitions of sodium orthophosphate Na_3PO_4 identified in our laboratory give thermal effects across the full composition range in the system $Na_3Ce(PO_4)_2$–Na_3PO_4. Transitions α/β' and β/γ' are characterized by

strong thermal effects on the DTA curves. The other transitions occur in the form of weak effects.

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