JOURNAL OF SOLID STATE CHEMISTRY 95, 265–269 (1991)

The System $LaPO_4$–K_3PO_4

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Received October 18, 1990

The phase diagram of system $LaPO_4$–K_3PO_4 has been determined by differential thermal, X-ray, and microscopic methods. The system contains only one intermediate compound, $K_3La(PO_4)_2$, which melts incongruently at 1500°C. This compound is stable down to room temperature and exhibits a polymorphic transition at 1215°C. It was confirmed that the low-temperature modification of this compound has a monoclinic unit cell with parameters a = 9.632(5), b = 5.660(2), and c = 7.514(3) Å; α = 90°, β = 90.55(3)°, and γ = 90°; V = 409.62 Å^3.

Introduction

The present study is the next step in our investigations on potassium–lanthanum phosphates. The research has been carried out for several years and was started because of the great interest in these compounds as new luminophore and laser materials. Until now, phase equilibria in that part of the system La_2O_3–K_2O–P_2O_5 which is rich in P_2O_5, i.e., within the composition range $La(PO_3)_3$–KPO_3–P_2O_5, have been examined in this laboratory (*1, 2*). Phase equilibria in the system $LaPO_4$–KPO_3–$La(PO_3)_3$ have been investigated as well, and its phase diagram has been determined (*3*). The present paper reports the results of our examinations on the binary system $LaPO_4$–K_3PO_4. Its phase diagram has not been determined so far. Literature data show that double potassium–lanthanum orthophosphate $K_3La(PO_4)_2$ is known. This compound, according to its composition, occurs in the system $LaPO_4$–K_3PO_4 (as an intermediate compound). Reference (*4*) reports that $K_3La(PO_4)_2$ has a monoclinic unit cell with the parameters: a = 9.59, b = 5.66, and c = 7.49 Å; β = 91.16°.

The alkali metal–lanthanide orthophosphates have interesting properties. Numerous literature sources report the existence of two types of binary 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). Both types of these compounds, according to their composition, can occur in the systems $M^{III}PO_4$–$M^{I}_3PO_4$.

Experimental

The samples in the binary system $LaPO_4$–K_3PO_4 were prepared from lanthanum orthophosphate $LaPO_4$ and potassium orthophosphate K_3PO_4. The following starting materials were used for synthesis of the orthophosphates: $La(NO_3)_3$ (Fluka), H_3PO_4 85% analytical grade, and $K_3PO_4 \cdot 3H_2O$ analytical grade.

Lanthanum orthophosphate $LaPO_4$ was obtained from the following solution: 0.4

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wt% of La_2O_3 (as $La(NO_3)_3$), 15 wt% of P_2O_5 (as H_3PO_4), and 84.6 wt% of distilled water (5). Potassium orthophosphate K_3PO_4 was obtained from $K_3PO_4 \cdot 3H_2O$ by heating at 900°C for 1 hr.

The investigations were carried out by differential thermal analysis (heating), powder X-ray diffraction, and microscopy in reflected light. Molten and sintered samples were used for thermal analysis. The high temperature thermal studies above 1400°C were performed in a horizontal resistance furnace with molybdenum winding, under argon. The test samples were presynthesized by the reaction in the solid phase. The initial components were mixed in the appropriate ratios, ground, pelletized, placed in platinum crucibles, sintered at 1000–1100°C, and then fused. Temperatures above 1400°C were measured by means of an optical pyrometer, which was calibrated against the melting points of Na_3PO_4 and $Ca_3(PO_4)_2$. In the thermal analysis a derivatograph type 3427 (MOM, Hungary) was used within the temperature range 20–1400°C. Temperatures were established by means of a Pt/Pt 10 Rh thermocouple, which was calibrated against the melting point of $Ca_2P_2O_7$, K_2SO_4, and the transition point of K_2SO_4 (583°C).

The phase purity of the reagents and the phase structure of the products were studied by powder X-ray diffraction. The powder X-ray analysis was performed on an HZG-4 diffractometer with Cu$K\alpha$ radiation.

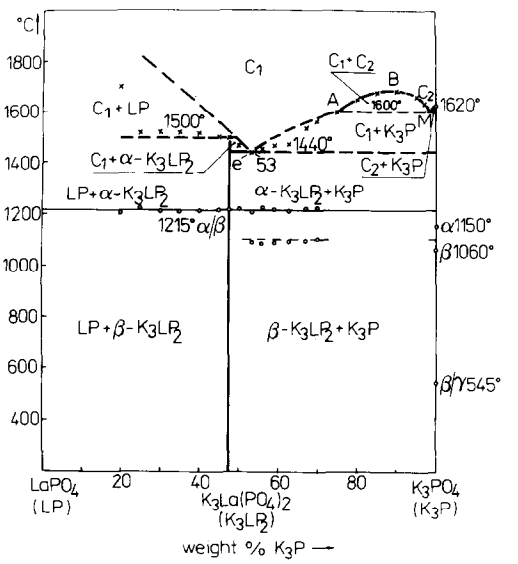

FIG. 1. Phase diagram of the system $LaPO_4$–K_3PO_4: ●, thermal analysis; x, optical. C = liquid.

Results and Discussion

Figure 1 shows the phase diagram of the system $LaPO_4$–K_3PO_4 determined within the temperature range 20–1800°C.

Samples from this system melt at high temperatures (above 1400°C). Therefore, the liquidus and solidus curves were estimated by observing the behavior of pellets in a horizontal furnace and by reading temperatures with the use of an optical pyrometer. Equilibria in the solid phase were determined by thermal analysis on heating molten and sintered samples. Thermal and microscopic examinations showed that there is only one intermediate compound in the system. It is formed at the 1 : 1 molar ratio $LaPO_4$: K_3PO_4 (52.42 wt% of $LaPO_4$, 47.58 wt% of K_3PO_4); i.e., $K_3La(PO_4)_2$. This double orthophosphate melts peritectically at approx. 1500°C. During differential thermal analysis of a sintered sample of stoichiometric composition of this compound, a very strong thermal effect appears on the DTA curve at 1240°C. With a molten sample, an analogous strong effect appears at 1215°C. This effect occurs in the system under investigation over the full examined composition range. We suppose it results from the polymorphic transition α/β-$K_3La(PO_4)_2$. The high-temperature modification (α) cannot be stabilized at room temperature by fast cooling in air or in ice.

The low-temperature modification, β-

$K_3La(PO_4)_2$, was investigated with X-ray diffraction. X-ray powder data were carefully measured using a Guinier-de Wolff focusing camera (Cu$K\alpha$ radiation, $\bar{\lambda}$ = 1.54184Å) and a powder X-ray diffractometer. The positions of the individual lines were determined from Guinier photographs. They were corrected and LSQ refined (α-Al_2O_3 being used as internal standard). Indexing was performed on the basis of the results of locally modified exhaustive procedures (*6*) and Ito's algorithm (*7*). After the effective splitting procedure had been applied to the diffraction pattern (*8*) and the intensities (*9*) had been compared with those predicted for the isomorphous replacement, the unit cell parameters were refined utilizing the uniquely ascribed peak positions. It was found that the low-temperature modification, β-$K_3La(PO_4)_2$, has a monoclinic structure (lattice type *P*), and cell parameters a = 9.632(5), b = 5.660(2), and c = 7.514(3) Å; α = 90°, β = 90.55(3)°, and γ = 90°; V = 409.62 Å^3. Table I presents the powder X-ray diffraction data of β-$K_3La(PO_4)_2$.

$K_3La(PO_4)_2$ can be obtained by a solid state reaction when an equimolar mixture of the initial orthophosphates is sintered at 1100°C for 20 hr. This phosphate can be also formed by melting and then slow cooling of this mixture.

Literature reports vary on the subject of polymorphic transitions of potassium orthophosphate K_3PO_4. Therefore, in 1981 (*10*) it was reexamined in our laboratory by thermal, dilatometric, and X-ray methods. The molten and sintered K_3PO_4 was investigated during cooling and heating. The results obtained indicate that K_3PO_4 exists in three polymorphic modifications. Transition temperatures in the molten compounds during cooling are as follows: α/β, 1066–1051°C and β/γ, 545°C; during heating: α/β, 1060–1150°C).

In the system $LaPO_4$–K_3PO_4, on the DTA curves during the heating of molten samples within the composition range 50–70 wt% of K_3PO_4, a not very strong thermal effect occurs at 1100°C. This effect does not appear in the part of the system rich in K_3PO_4. There are also no effects connected with the transition β/γ-K_3PO_4. X-ray analysis of molten samples in the part of the system which is rich in potassium orthophosphate showed only the presence of the high-temperature modification α-K_3PO_4 and small quantities of β-$K_3La(PO_4)_2$. X-ray and thermal examinations (the distribution of melting points) of samples, within the composition range 75–100 wt% of K_3PO_4, show that there is a limited solubility of the components in the liquid state above approx. 1600°C. It is manifested by the separation of the liquid into two liquid solutions, C_1 and C_2. Over point B (Fig. 1), above the liquidus curve, there is a field of stability of liquid solutions with unlimited mutual solubility of components. In the ABM field, there is the stable mixture of liquid solutions, C_1 and C_2. On the left of this field, over the liquidus curve, there is a monophase field of stability of liquid solution C_1, and on the right there is a monophase field of stability of liquid solution C_2. Between the liquidus curve and the solidus curve, there are two phase fields. At point M (called a monotectic point), at the constant temperature of approx. 1600°C (monotectic temperature), a monotectic reaction proceeds as follows: $C_{2M} \rightarrow K_3PO_4 + C_{1A}$ (where: C_{2M} = liquid C_2 with the composition of point M, C_{1A} = liquid C_1 with the composition corresponding to point A).

According to Fig. 1, in the system $LaPO_4$–K_3PO_4, a eutectic occurs at the content of 53 wt% of K_3PO_4, at 1440°C. The peritectic reaction, which proceeds according to the formula $C + LaPO_4 \rightarrow K_3La(PO_4)_2$, ends at approx. 50 wt% of K_3PO_4.

Potassium orthophosphate K_3PO_4 is very hygroscopic. Therefore samples rich in K_3PO_4 absorb moisture easily. Hence, microscopic observations in reflected light

TABLE I

X-RAY ANALYSIS DATA FOR β-$K_3La(PO_4)_2$ MODIFICATION

hkl	$d_{obs.}$(Å)	$d_{calc.}$(Å)	Intensities
001	7.47	7.50	52
101	5.86	5.87	1
110	4.87	4.88	28
200	4.80	4.81	8
11$\bar{1}$	4.09	4.10	10
111	4.07	4.08	75
20$\bar{1}$		4.08	
210	3.664	3.664	5
21$\bar{1}$	3.307	3.309	15
211	3.277	3.277	34
300	3.207	3.205	1
11$\bar{2}$	2.984	2.986	100
20$\bar{2}$		2.981	
112	2.961	2.962	83
30$\bar{1}$		2.965	
202	2.935	2.935	24
301		2.930	
020	2.827	2.831	68
310	2.792	2.789	79
021	2.649	2.649	3
31$\bar{1}$	2.629	2.627	5
212	2.605	2.606	4
311		2.602	
30$\bar{2}$	2.459	2.457	6
10$\bar{3}$	2.431	2.430	14
103	2.410	2.411	6
221	2.315	2.314	16
40$\bar{1}$	2.301	2.300	7
013	2.290	2.288	4
022	2.260	2.260	7
11$\bar{3}$	2.235	2.233	15
20$\bar{3}$		2.234	
122	2.195	2.195	9
41$\bar{1}$	2.134	2.131	14
411	2.116	2.114	9
22$\bar{2}$	2.053	2.053	24
213		2.054	
222	2.037	2.038	43
321		2.036	
40$\bar{2}$		2.039	
303	1.959	1.957	9
023	1.874	1.874	13
004		1.876	
31$\bar{3}$		1.875	
32$\bar{2}$	1.858	1.856	18
501		1.856	
130	1.850	1.852	6
313		1.849	
123	1.837	1.836	6
322		1.838	
104		1.836	
131	1.797	1.797	10
421	1.777	1.775	2
511		1.776	
230	1.757	1.757	14
11$\bar{4}$		1.756	
20$\bar{4}$		1.757	
41$\bar{3}$	1.671	1.670	12
13$\bar{2}$	1.663	1.663	12
214		1.662	
132	1.658	1.659	10
413	1.647	1.645	8
51$\bar{2}$		1.648	
330	1.627	1.626	16
32$\bar{3}$		1.627	
512		1.628	
323	1.611	1.610	4
23$\bar{2}$	1.593	1.595	6
33$\bar{3}$		1.592	
520		1.591	
43$\bar{1}$	1.459	1.459	5
612		1.418	1

Note. Monoclinic system: a = 9.632(5), b = 5.660(2), and c = 7.514(3) Å; α = 90°, β = 90.55(3)°, and γ = 90°; V = 409.62 Å^3.

could be performed only with samples rich in $LaPO_4$.

Acknowledgments

The authors thank Dr. J. Matuszewski for his extensive help in the X-ray experiments. This paper was included in the CPBP-01.18 problem and was financially supported by the Ministry of National Education.

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