Phase Equilibrium Relations in the Binary Systems $LiPO_3$–CeP_3O_9 and $NaPO_3$–CeP_3O_9

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The $LiPO_3$–CeP_3O_9 and $NaPO_3$–CeP_3O_9 systems have been investigated for the first time by DTA, X-ray diffraction, and infrared spectroscopy. Each system forms a single 1:1 compound. $LiCe(PO_3)_4$ melts in a peritectic reaction at 980°C. $NaCe(PO_3)_4$ melts incongruently, too, at 865°C. These compounds have a monoclinic unit cell with the parameters: $a = 16.415(6)$, $b = 7,042(6)$, $c = 9.772(7)$ Å; $\beta = 126.03(5)°$; $Z = 4$; space group C_2/c for LiCe $(PO_3)_4$; and $a = 9.981(4)$, $b = 13.129(6)$, $c = 7.226(5)$ Å, $\beta = 89.93(4)°$, $Z = 4$, space group $P2_1/n$ for $NaCe(PO_3)_4$. It is established that both compounds are mixed polyphosphates with chain structure of the type $|M_I^I\ M_{II}^{III}\ (PO_3)_4|_\infty$ M_I^I: alkali metal, M_{II}^{III}: rare earth.

Recently, widespread attention has been given to double condensed phosphates of rare earths and alkali metals, which are promising materials for quantum electronics. The literature gives no information on the interaction of alkali metal metaphosphates with CeP_3O_9. Continuing previous work (*1*), we present the current results for a study of the $LiPO_3$–CeP_3O_9 and $NaPO_3$–CeP_3O_9 systems.

Experimental

Lithium (*2*) and sodium (*3*) metaphosphates were made by complete dehydration of analytical-reagent-grade monosubstituted dihydrogen phosphates, followed by fusion and holding in the molten state ($LiPO_3$ for 1 hr at 700°C and $NaPO_3$ for 4 hr at 720°C). The cerium trimetaphosphate $CeP_3O_9 \cdot 3H_2O$ was made as described earlier (*4*).

Samples were mixed with the desired composition ratios, pounded several times and reacted in porcelain crucible for several days at 600°C in the case of $LiPO_3$–CeP_3O_9 mixture and at 550°C in the case of the $NaPO_3$–CeP_3O_9 mixture. For the CeP_3O_9-rich compositions, the mixtures were precalcined either at 940°C (first system) or at 800°C (second system).

The equilibrium diagrams was established by differential thermal analysis (DTA) on an M5 Micro DTA Setaram apparatus, by recording the heating curves of specimens that were fused in platinium crucibles. Pt/Pt–Rh thermocouples calibrated against the melting point of NaCl were used to detected thermal anomalies. Heating rate of the furnace was 10°C/min and α-Al_2O_3 was used as a reference. The accuracy of temperature measured from DTA was about ±5°C below 1000°C and ±10°C above this temperature.

The initial components and the new phases formed in the two systems were

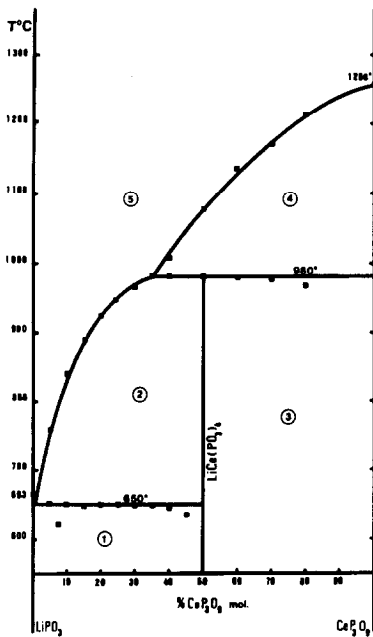FIG. 1. Equilibrium diagram of the $LiPO_3$–CeP_3O_9 system: (1) $LiPO_3$ + $LiCe(PO_3)_4$; (2) $LiCe(PO_3)_4$ + CeP_3O_9; (3) liquid + $LiCe(PO_3)_4$; (4) liquid + CeP_3O_9; (5) liquid.
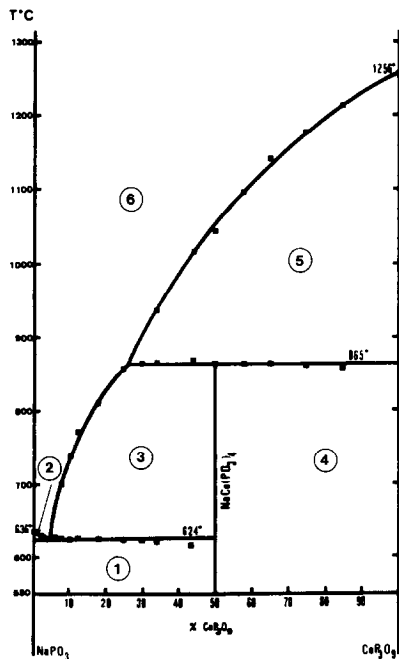
FIG. 2. Equilibrium diagram of the $NaPO_3$–CeP_3O_9 system: (1) $NaPO_3$ + $NaCe(PO_3)_4$; (2) $NaPO_3$ + liquid; (3) liquid + $NaCe(PO_3)_4$; (4) $NaCe(PO_3)_4$ + CeP_3O_9; (5) CeP_3O_9 + liquid; (6) liquid.

identified by X-ray diffraction on a Noreclo Philips diffractometer with nickel-filtered copper radiation. Sample powders tamped in the sample holder were used.

The ir absorption spectra were recorded on a IR- 377 Perkin–Elmer spectrophotometer using pellets formed by mixing the specimens with KBr.

TABLE I

X-RAY ANALYSIS DATA FOR $LiCe(PO_3)_4$

$h\,k\,l$	d_{obs} (Å)	d_{calc} (Å)	I
2 0 0	6.61	6.64	80
$\bar{1}$ 1 1	5.70	5.71	30
$\bar{2}$ 0 2	4.87	4.88	11
$\bar{3}$ 1 1	4.32	4.32	95
$\bar{4}$ 0 2	3.92	3.92	100
$\bar{3}$ 1 2	3.83	3.83	35
3 1 0	3.73	3.75	16
0 2 0	3.53	3.52	8
4 0 0	3.31	3.32	10
0 2 1 $\bar{2}$ 2 1	3.22	3.22 3.21	40
2 2 0	3.11	3.11	15
$\bar{5}$ 1 2 $\bar{3}$ 1 3	2.959	2.963 2.956	40
$\bar{5}$ 1 1	2.863	2.863	50
$\bar{6}$ 0 2	2.738	2.734	70
$\bar{1}$ 1 3	2.706	2.709	16
2 2 1	2.656	2.656	14
0 2 2	2.626	2.629	25
5 1 0	2.481	2.484	4
$\bar{4}$ 0 4	2.448	2.443	6
4 2 0	2.417	2.415	10
$\bar{2}$ 2 3	2.359	2.356	9
1 3 0	2.318	2.312	16
$\bar{2}$ 0 4	2.299	2.299	13
$\bar{6}$ 0 4 $\bar{1}$ 3 1	2.285	2.286 2.282	15
1 1 3 6 0 0	2.213	2.216 2.212	35
2 2 2	2.167	2.171	14
0 2 3	2.107	2.109	11
$\bar{6}$ 2 3	2.098	2.098	9
4 2 1 3 3 0	2.071	2.075 2.074	13
$\bar{6}$ 2 1 5 1 1	2.063	2.069 2.067	20
$\bar{1}$ 1 4	2.050	2.053	10

TABLE II

X-Ray Analysis Data for NaCe(PO₃)₄

hkl	d_{obs} (Å)	d_{calc} (Å)	I	hkl	d_{obs} (Å)	d_{calc} (Å)	I
0 2 0	6.55	6.56	45	1 3 2	2.686	2.684	6
1 0 1 $\bar{1}$ 0 1	5.85	{5.86 5.85}	9	$\bar{1}$ 3 2	2.683	2.683	6
2 0 0	4.99	4.99	7	2 2 2	2.671	2.674	4
2 1 0	4.67	4.67	7	$\bar{2}$ 2 2	2.662	2.662	3
1 2 1 $\bar{1}$ 2 1	4.37	{4.37 4.37}	17	3 3 0	2.649	2.649	8
2 2 0	3.98	3.97	100	2 4 1 $\bar{2}$ 4 1	2.564	{2.564 2.563}	4
2 1 1 $\bar{2}$ 1 1	3.91	{3.92 3.92}	9	1 5 0	2.539	2.539	7
0 3 1	3.74	3.74	5	4 0 0 3 3 1 $\bar{3}$ 3 1	2.495	{2.495 2.488 2.486}	5
1 3 1 $\bar{1}$ 3 1	3.51	{3.51 3.50}	8	0 5 1	2.468	2.468	3
2 3 0 1 1 2	3.30	{3.29 3.29}		2 3 2 $\bar{2}$ 3 2 0 4 2	2.432	{2.434 2.432 2.429}	5
$\bar{1}$ 1 2 0 4 0	3.29	{3.29 3.28}	9	3 1 2 $\bar{3}$ 1 2	2.409	{2.407 2.405}	2
3 1 0	3.23	3.23	10	1 5 1 $\bar{1}$ 5 1	2.396	{2.396 2.396}	3
0 2 2	3.16	3.17	6	1 0 3 $\bar{1}$ 0 3 3 4 0 4 2 0	2.341	{2.342 2.341 2.337 2.333}	8
1 4 0	3.10	3.12	5	1 1 3 $\bar{1}$ 1 3	2.309	{2.306 2.304}	2
3 0 1 $\bar{3}$ 0 1 1 2 2 $\bar{1}$ 2 2	3.03	{3.02 3.02 3.02 3.02}	10	3 2 2 $\bar{3}$ 2 2	2.305	{2.295 2.292}	
2 3 1 $\bar{2}$ 3 1 0 4 1	2.990	{2.995 2.994 2.988}	9	3 4 1 $\bar{3}$ 4 1 4 2 1 $\bar{4}$ 3 1 2 5 1 $\bar{2}$ 5 1	2.217	{2.224 2.223 2.221 2.219 2.213 2.212}	7
3 1 1 $\bar{3}$ 1 1	2.944	{2.946 2.944}	5				
2 0 2	2.926	2.928	5				
$\bar{2}$ 0 2	2.920	2.925	5				
1 4 1 $\bar{1}$ 4 1	2.862	{2.863 2.862}	9				
3 2 1 $\bar{3}$ 2 1 2 4 0	2.745	{2.746 2.744 2.742}	45				

Results and Discussion

The results of the thermal analysis of the two systems:

(I) LiPO₃–CeP₃O₉

(II) NaPO₃–CeP₃O₉

are given in Fig. 1 and Fig. 2.

The components of each system form a 1:1 definite compound. Both compounds, LiCe(PO₃)₄ and NaCe(PO₃)₄, decompose on heating in a peritectic reaction at 980 and 865°C, respectively. For system I, the branches of the liquidus curve intersect at a nonvariant peritectic point at 37% CeP₃O₉, the eutectic level occurs at 650°C. For system II, the nonvariant peritectic point is at 27% CeP₃O₉ and the eutectic temperature is 624°C, the nonvariant eutectic point corresponds to a concentration of 5% CeP₃O₉.
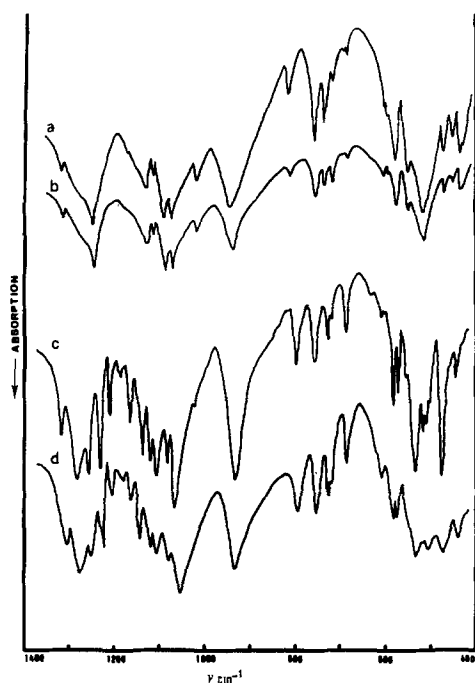
The individuality of the definite com-

FIG. 3. Infrared absorption spectra of (a) LiCe(PO₃)₄; (b) LiNd(PO₃)₄; (c) NaCe(PO₃)₄; (d) NaNd(PO₃)₄.

pounds was established by X-ray diffraction (Tables I, II). The diffraction pattern of a specimen with the compositions 50%–50% differs from those of the original components. $LiCe(PO_3)_4$ is isotypic with $LiNdP_4O_{12}$ (5) and $NaCe(PO_3)_4$ is isotypic with $NaNdP_4O_{12}$ (6). Indexing of the compounds X-ray diffraction patterns by the Hess–Lipson method (7) established that the compounds have a monoclinic unit cell with the following parameters: $a = 16.415$ (6), $b = 7.042$ (6), $c = 9.772$ (7) Å, $\beta = 126.03$ (5)° and $Z = 4$ for $LiCe(PO_3)_4$; $a = 9.981$ (4), $b = 13.129$ (6), $c = 7.226$ (5) Å, $\beta = 89.93$ (4)° and $Z = 4$ for $NaCe(PO_3)_4$. Their space groups are $C2/c$ and $P2_1/n$, respectively.

A comparaison of the vibrational spectra of $LiCe(PO_3)_4$ with that of $LiNd(PO_3)_4$[1] and of $NaCe(PO_3)_4$ with that of $NaNd(PO_3)_4$[1] in

¹ These compounds were prepared from reagent grade Nd₂O₃, NH₄H₂PO₄ and the suitable carbonate.

Fig. 3 suggests that each of the Ce-containing compounds is isostructural with its Nd-containing analog. Interpreted according to the same principles as in previous investigations (8, 9), these spectra are characteristic and differ from those of cyclic metaphosphates (10) by their distinctive absorption in the regions of the stretching and deformation vibrations of the PO₂ and POP bonds. Both groups of absorption bands at 450–480 cm⁻¹ and 500–600 cm⁻¹ and the multiplet at 650–810 cm⁻¹ are typical of chain polyphosphates (9–11). Likewise, the number of the others bands, their positions and relative intensities in each quasi-characteristic region for the P–O stretching vibrations of the Ce-containing compounds or compared to that of Nd-containing compounds establisher grounds for asserting that the most probable form of the anion in these compounds is a chain structure with PO₄ tetrahedra in a identity period, similarly to $LiNd(PO_3)_4$ (5) and $NaNd(PO_3)_4$ (6).

Acknowledgment

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