ELSEVIER

Thermochimica Acta 370 (2001) 125–128

thermochimica acta

www.elsevier.com/locate/tca

The system $CePO_4$–K_3PO_4

Irena Szczygiel*

Department of Inorganic Chemistry, Faculty of Engineering and Economics, Wroclaw University of Economics,
ul. Komandorska 118/120, 53-345 Wroclaw, Poland

Received 4 October 2000; received in revised form 22 November 2000; accepted 12 December 2000

Abstract

The phase diagram of the system $CePO_4$–K_3PO_4 has been determined based on investigations by differential thermal analysis, X-ray powder diffraction, IR spectroscopy and optical microscopy. The system contains only one intermediate compound $K_3Ce(PO_4)_2$, which melts incongruently at (1500 ± 20)°C. This compound is stable down to room temperature and exhibits a polymorphic transition at 1180°C. It was confirmed that the low-temperature form β-$K_3Ce(PO_4)_2$ crystallizes in a monoclinic system, space group $P2_1/m$ with unit cell parameters $a = 9.579$ (5), $b = 5.634$ (6), $c = 7.468$ (5) Å; $\alpha = \gamma = 90°$, $\beta = 90.81$ (3)°; $V = 403.083$ Å^3. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cerium orthophosphate; Potassium orthophosphate; Phase diagram; X-ray analysis

1. Introduction

In recent years, double and triple phosphates with the general formulae $M^I_3Ln(PO_4)_2$ and $M^IM^{II}Ln(PO_4)_2$ (where M^I denotes an alkali metal, M^{II} an alkaline earth metal and Ln is a rare earth element) have gained increasing attention [1–9]. Lanthanide phosphates have been examined with respect to their luminescence properties [2] and energy transfer phenomena [3], for use as new luminophore and laser materials, as ionic conductors, as hosts for actinide ions and for other possible applications.

Double orthophosphates $M^I_3Ln(PO_4)_2$, according to their composition, could occur in the ternary systems Ln_2O_3–M_2O–P_2O_5 on the binary sections M_3PO_4–$LnPO_4$. Binary and ternary systems, including rare earth phosphates as well as phosphates of alkali metals and of alkaline earth elements, have been investigated in our laboratory for a number of years. In the present paper, the results of investigations of the binary system $CePO_4$–K_3PO_4 are described. Its phase diagram has not been reported. Even so, an intermediate orthophosphate of $K_3Ce(PO_4)_2$ has been reported [7–9].

Potassium-rare earth orthophosphates are usually synthesized by solid state reactions. Bamberger et al. [8,9] prepared $K_3Ce(PO_4)_2$ by firing mixtures of K_3PO_4 and $CePO_4$ to 500°C in air, followed by further calcination at 950°C in flowing helium. Letho et al. [7] obtained $K_3Ce(PO_4)_2$ by heating a mixture of $CePO_4$, KNO_3 and $NH_4H_2PO_4$ (mole ratios 1:3:1) at 1000°C for 24 h. $K_3Ce(PO_4)_2$ has a monoclinic unit cell ($P2_1/m$) with the parameters $a = 9.621$ (1), $b = 5.656$ (3), $c = 7.496$ (1) Å; $\beta = 90.6$ (1)° [7]. The compound is isotypic with $K_3Nd(PO_4)_2$.

2. Experimental

The following initial reagents were used: $Ce(NO_3)_3\cdot 6H_2O$, $NH_4H_2PO_4$ and $K_3PO_4\cdot 3H_2O$, all analytically pure. The samples in the binary system $CePO_4$–K_3PO_4

---

* Tel.: +48-71-367-28-53; fax: +48-71-368-02-92.
E-mail address: szczygl@credit.ae.wroc.pl (I. Szczygiel).

0040-6031/01/$ – see front matter
PII: S0040-6031(00)00775-9

were prepared from cerium orthophosphate $CePO_4$ and potassium orthophosphate K_3PO_4. Cerium orthophosphate $CePO_4$ was obtained from $Ce(NO_3)_3{\cdot}6H_2O$ and $NH_4H_2PO_4$ by the method described in [8]. Potassium orthophosphate K_3PO_4 was obtained from $K_3PO_4{\cdot}3H_2O$ by dehydration at 900°C for 1 h.

The phase investigation was carried out by differential thermal analysis (DTA) during heating, powder X-ray diffraction, infrared (IR) spectroscopy and optical microscopy. The DTA-heating was carried out by means of a derivatograph-type 3427 (MOM, Hungary) within temperature range 20–1400°C with heating rate 10°C/min. Platinum crucibles and air atmosphere were used. High purity Al_2O_3 was used as the standard substance. Temperatures were read by means of a Pt/Pt10Rh thermocouple, which was calibrated against the melting points of $Ca_2P_2O_7$ (1353°C), K_2SO_4 (1070°C) and NaCl (801°C). The high-temperature thermal studies above 1400°C was carried out in an atmosphere of argon in a horizontal, resistance furnace with molybdenum winding. Temperature were read by means of an optical pyrometer, which was calibrated against the melting points of Na_3PO_4 (1583°C) and $Ca_3(PO_4)_2$ (1810°C). The examined samples were pressed into pellets, placed in platinum boats, sintered at 900°C for 20 h and then fused. The quenching technique was also used for phase determination. The obtained phases were identified by powder X-ray analysis at room temperature on an HZG-4 diffractometer (Cu Kα radiation) and a Siemens D 5000 diffractometer (Cu Kα radiation, Ni filter, scintillating counter). The EVA software (DIFFRACT PLUS package) was applied to process the experimental spectra (including background removing, smoothing, $K\alpha_2$ stripping and peak finding). The PDF-2 data base (ICDD) was searched to detect the phases present in the samples (with the restricting condition that they must include the following elements K, Ce, P and O). The phase purity of the reagents and phase composition of the alloys were controlled microscopically. Microsections were prepared from molten and crystallized samples, which were polished and examined

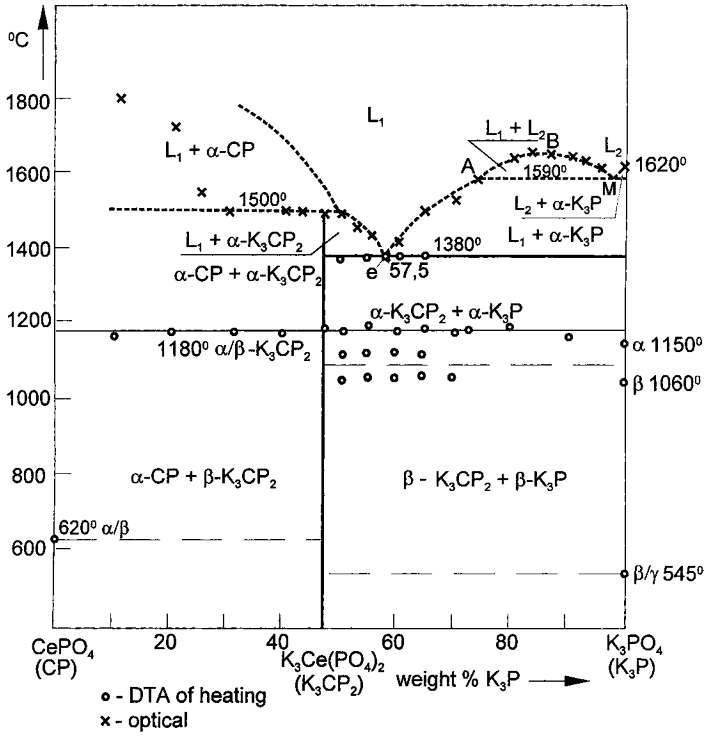

Fig. 1. The phase diagram of the binary system $CePO_4$–K_3PO_4.

optically. IR spectra were measured over the range 1400–400 cm^{-1} (with KBr as diluent) with a Specord M-80 spectrophotometer (Carl Zeiss, Jena).

3. Results and discussion

The phase diagram of the binary system $CePO_4$–K_3PO_4, which is presented in Fig. 1, has been determined in the whole range of composition and up to $t = 1800°C$. The samples from this system are high-melting (above 1400°C). Liquids and solids curves are determined by optical pyrometer. Solid state equilibria were determined by DTA during heating sintered samples and also molten and crystallized samples.

It has been found that the initial orthophosphates form one intermediate compound with molar ratio $CePO_4$:K_3PO_4 = 1:1 (47.45 wt.% K_3PO_4, 52.55 wt.% $CePO_4$) and formula $K_3Ce(PO_4)_2$. The compound melts incongruently at ~1500°C and it is stable to room temperature. It follows from DTA and X-ray analysis that $K_3Ce(PO_4)_2$ appears in two polymorphic modifications. The transition between α- and β-$K_3Ce(PO_4)_2$ takes place at $t = 1180°C$ and is accompanied by a very strong thermal effect on the DTA-curve. The effect occurs in the entire range of composition in the system $CePO_4$–K_3PO_4.

It is not possible to stabilize the high-temperature form, α-$K_3Ce(PO_4)_2$, at room temperature by ice quenching. X-ray studies of the low-temperature form, β-$K_3Ce(PO_4)_2$, have shown no phases, except for $K_3Ce(PO)_4$, which matches the experimental pattern. The PROSZKI software [11] exploiting procedure named APPLE (LSQ refinement) [12] was used to refine lattice parameters. The indexing of the reflections are given in Table 1.

The low-temperature phase β-$K_3Ce(PO_4)_2$ crystallizes in the monoclinic (β-unique) system ($P2_1/m$ space group) with the parameters $a = 9.579$ (5), $b = 5.634$ (6), $c = 7.468$ (5) Å; $\alpha = \gamma = 90°$, $\beta = 90.81$ (3)°; $V = 403.083$ Å^3 in accordance with data given in [7]. The IR spectrum of β-$K_3Ce(PO_4)_2$, within the range 1400–400 cm^{-1}, is given in Fig. 2.

In our laboratory it was found that pure $K_3Ce(PO_4)_2$ can be obtained through the solid state reaction by sintering an equimolar mixture of the parent phosphates at a temperature of 900°C for 20 h. This phosphate also is formed as a result of the slow cooling of a fused, equimolar mixture of $CePO_4$ and K_3PO_4.

Table 1
X-ray analysis data for β-$K_3Ce(PO_4)_2$ modyfication

	h k l	Intensities	d_{obs} (Å)	d_{calcs} (Å)
1	1 0 0	5.7	9.51500	9.57851
2	0 0 1	75.4	7.43154	7.46778
3	$\bar{1}$ 0 1	5.9	5.91320	5.93033
4	1 0 1	5.5	5.82691	5.84929
5	1 1 0	35.6	4.84401	4.85660
6	2 0 0	9.7	4.77546	4.78925
7	$\bar{1}$ 1 1	34.3	4.07394	4.08480
8	$\bar{2}$ 0 1	79.7	4.05081	4.05768
9	2 0 1	3.4	3.99893	4.00569
10	2 1 0	5.4	3.64359	3.64917
11	1 0 2	10.5	3.46329	3.46233
12	$\bar{2}$ 1 1	16.8	3.28975	3.29273
13	2 1 1	25.0	3.26092	3.26476
14	3 0 0	2.8	3.18863	3.19284
15	0 1 2	30.0	3.11477	3.11251
16	$\bar{1}$ 1 2	82.9	2.96729	2.97049
17	$\bar{3}$ 0 1	100.0	2.94873	2.95094
18	2 0 2	19.2	2.92095	2.92464
19	0 2 0	73.2	2.81602	2.81729
20	$\bar{3}$ 1 0	88.8	2.77684	2.77786
21	1 2 0	10.5	2.69816	2.70280
22	0 2 1	8.9	2.63524	2.63595
23	$\bar{3}$ 1 1	11.9	2.61375	2.61413
24	$\bar{1}$ 2 1	5.5	2.54430	2.54473
25	$\bar{3}$ 0 2	9.7	2.44483	2.44382
26	$\bar{1}$ 0 3	19.5	2.41828	2.41760
27	1 0 3	9.7	2.40033	2.40095
28	2 2 1	19.5	2.30397	2.30441
29	$\bar{4}$ 0 1	11.0	2.29112	2.28973
30	0 2 2	13.5	2.24900	2.24894
31	1 2 2	16.9	2.18581	2.18526
32	$\bar{4}$ 1 1	24.6	2.12216	2.12127
33	4 1 1	19.0	2.10651	2.10628
34	$\bar{3}$ 2 1	19.9	2.03884	2.03774
35	4 0 2	7.6	2.00430	2.00284
36	$\bar{3}$ 0 3	9.7	1.97747	1.97678
37	3 0 3	21.2	1.95022	1.94976
38	$\bar{4}$ 1 2	21.2	1.91063	1.90887
39	4 1 2	15.7	1.88751	1.88717
40	5 0 1	17.8	1.84858	1.84931
41	$\bar{1}$ 3 1	7.6	1.79082	1.79054
42	2 3 1	5.1	1.70111	1.70054
43	5 0 2	5.9	1.69570	1.69472
44	1 3 2	16.1	1.65222	1.65093
45	5 2 1	13.1	1.54662	1.54600

Investigations of the polymorphic transitions in the initial phosphates confirm that $CePO_4$ appears in two polymorphic modifications ($t_{trs} = 620°C$

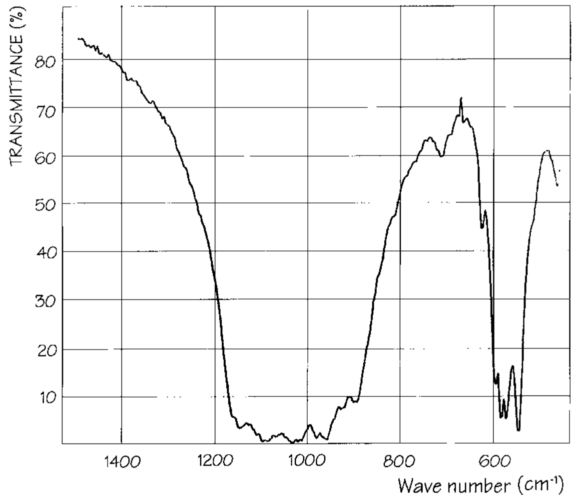

Fig. 2. IRS of β-$K_3Ce(PO_4)_2$.

[10]). Polymorphic transitions of potassium orthophosphate K_3PO_4 were investigated by many authors [13–15]. Znamierowska [15] re-examined molten and sintered K_3PO_4 during cooling and heating by thermal, dilatometric and X-ray methods. Obtained results indicate that K_3PO_4 melts congruently at 1620°C and appears in three polymorphic modifications. The transitions in molten K_3PO_4, as observed during cooling, take place at 1066–1051°C (α/β) and 545°C (β/γ). The α/β-K_3PO_4 transition during heating takes place in the temperature range 1060–1150°C.

The DTA-curves of the $CePO_4$–K_3PO_4 system show no thermal effects associated with the transition α/β-$CePO_4$, which is most likely subsequent to the inhibiting influence of $K_3Ce(PO_4)_2$. In contrast, for the composition range from 50–70 wt.% of K_3PO_4, the DTA-curves of molten samples reveal the thermal effects at 1060 and 1120°C (during heating), which are connected with the transition α/β-K_3PO_4. The effects are absent in the K_3PO_4-rich part of the system. The β/γ transition of K_3PO_4 is also not observed. This is most likely due to limited solubility of the components in the liquid state within the composition range 75–100 wt.% K_3PO_4, at high temperatures (∼1600°C). In this region liquid immiscibility is observed (cf. Fig. 1).The critical temperature (given by point B) is (1655 ± 20)°C. The monotectic temperature (given by point M) is (1590 ± 20)°C.

The eutectic occurs at 57.5 wt.% of K_3PO_4 at $t = 1380$°C. The composition of the liquid at the peritectic decomposition of $K_3Ce(PO_4)_2$ is ∼50 wt.% of K_3PO_4.

Potassium orthophosphate K_3PO_4 is a very hygroscopic compound. The samples rich in K_3PO_4 easily absorb moisture, which has been a serious obstacle during the course of investigations. Hence, microscopic observations could be realized only for the samples richer in $CePO_4$.

Acknowledgements

The author thanks Dr. P. Wilk for his help in the X-ray experiments.

References

[1] K.A. Gschneidner Jr. (Ed.), Industrial application of rare earth elements in ACS, Symp. Ser. 164 (1981).
[2] B. Finke, L. Schwarz, P. Gürtler, M. Kraas, M. Joppien, J. Becker, J. Luminescence 60/61 (1994) 975.
[3] A.M. Srivastava, M.T. Sobieraj, A. Valossis, S.K. Ruan, E. Banks, J. Electrochem. Soc. 137 (1990) 2959.
[4] H.Y.P. Hong, S.R. Chinn, Mater. Res. Bull. 11 (1976) 421.
[5] H. Wulff, B. Finke, L. Schwarz, Z. Phys. Chem. 262 (1981) 1155.
[6] L. Schwarz, B. Finke, G. Loos, J. Radioanal. Chem. 83 (1984) 83.
[7] J.Z. Letho, P. Houenou, R. Eholie, C. R. Acad. Sci. Ser. 2 (307) (1988) 1177.
[8] C.E. Bamberger, P.R. Robinson, R.L. Sherman, Inorg. Chim. Acta 34 (1979) L203.
[9] C.E. Bamberger, R.G. Haire, G.M. Begun, L.C. Ellingboe, Inorg. Chim. Acta 95 (1984) 49.
[10] I. Szczygiel, T. Znamierowska, J. Solid State Chem. 95 (1991) 260.
[11] W. Lasocha, K. Lewinski, PROSZKI-system of programs for powder diffraction data analysis, Ver 2.4, Jagielon University, Krakow, Poland.
[12] E. Appleman, H.T. Evans Jr., E. Handwerker, APPLEMAN-program for indexing and least squares unit cell refinement, freeware taken from Internet.
[13] G.A. Buhalova, I.V. Mardirosova, Z. Neorg. Khim. 12 (1967) 2825.
[14] A.W. Kolsi, Rev. Chim. Minerale 13 (1976) 416.
[15] T. Znamierowska, Polish J. Chem. 55 (1981) 747.