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Phase Equilibria in the System $CePO_4 – Ba_3(PO_4)_2$

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Based on thermal investigation and X-ray powder diffraction the unknown so far phase diagram of the binary system $CePO_4–Ba_3(PO_4)_2$ has been elaborated. It contains an intermediate compound $Ba_3Ce(PO_4)_3$, which congruently melts at about 2080°C, is stable down to room temperature and has an eulytite structure. In the composition range given by the molar ratio of $CePO_4{:}Ba_3(PO_4)_2$ from 1:1 to 1:6 there exist solid solutions of the eulytite structure. At high temperatures there exist two binary eutectics (t_{e_1} = 1840°C, t_{e_2} = 1600°C).

Key words: phase equilibria, barium-cerium phosphates, solid solutions

This work includes part of our investigations in the double phosphates of lanthanides (Ln^{III}) with alkali (M^{I}) and/or alkaline earth metals (M^{II}). According to many papers these compounds belong to the types:

$M^{I}_{3}Ln^{III}(PO_4)_2$, $M^{I}_{3}Ln^{III}_{2}(PO_4)_3$, $M^{II}_{3}Ln^{III}(PO_4)_3$.

Phosphates of the formula $M^{II}_{3}Ln^{III}(PO_4)_3$ and eulytite structure are of great interest. They are of practical use mainly in the of optics and optoelectronics. According to their composition, the phosphates $M^{II}_{3}Ln^{III}(PO_4)_3$ appear in the systems $M^{II}_{3}(PO_4)_2–Ln^{III}PO_4$. Now we present the results of investigation of a binary system $CePO_4–Ba_3(PO_4)_2$, whose phase diagram was unknown. According to [1,2] there exist two double orthophosphates of barium and cerium of the formulas $Ba_3Ce(PO_4)_3$ and $Ba_7Ce(PO_4)_6$. Both compounds crystallize in the regular system and are isomorphous with the eulytite $Bi_4(SiO_4)_3$. The lattice parameter *a* of the $Ba_3Ce(PO_4)_3$ phosphate is 10.511 Å and that of $Ba_7Ce(PO_4)_6$ is 10.551 Å.

EXPERIMENTAL

Samples for investigation of the $CePO_4–Ba_3(PO_4)_2$ system were obtained from parent orthophosphates. These reagents were synthesized from the ready reagents of analytical purity: $BaCO_3$, $BaHPO_4$, $Ce(NO_3)_3{\cdot}6H_2O$, $NH_4H_2PO_4$.

Phosphate $Ba_3(PO_4)_2$ was synthesized from a mixture of 1 mole $Ba_2P_2O_7$ and 1 mole $BaCO_3$ by sintering at 1300°C for 6 h. Barium diphosphate $Ba_2P_2O_7$ was obtained by a complete dehydratation of $BaHPO_4$ at 900°C for 1 h. Cerium orthophosphate $CePO_4$ was obtained from $Ce(NO_3)_3{\cdot}6H_2O$ and $NH_4H_2PO_4$ by the method described in [3].

Samples for thermal study were synthesized by the conventional method of solid state reaction. Parent substances were weighed in the presumed amounts, thoroughly mixed, grated for homogenization in an agate mortar, then presynthesized by sintering in air. Conditions for the synthesis were experimentally established. Driving at the equlibrium state was monitored by phase X-ray analysis and differential thermal analysis (DTA).

The phase diagram of the $CePO_4$–$Ba_3(PO_4)_2$ binary system in the subsolidus region (below 1450°C) was elaborated based on DTA results (heating; cooling) and powder X-ray diffraction. DTA of heating was performed by using a derivatograph type C (MOM, Hungary) over the temperature range 20–1400°C (the heating rate 5°/min; platinum crucible; weight of a sample 0.2 to 0.7 g). The standard substance was of high-purity Al_2O_3. DTA of cooling (beginning with 1450°C) was carried out in a home-made resistance furnace with a winding of PtRh30 (under air atmosphere, weight of one sample about 3 g). Temperature, in DTA investigation (both heating and cooling), was determined by thermocouple Pt/PtRh10, calibrated against the melting points of $Ca_2P_2O_7$ (1353°C), K_2SO_4 (1070°C), NaCl (801°C) and the polymorphic transformation point K_2SO_4 (583°C).

High temperature thermal examination (above 1450°C) was carried out in argon in home-made horizontal resistance furnaces with a molybdenum winding or a tungsten pipe. The samples were obtained by pressing into pellets, sintering (presynthesis) and fused. Temperature was read by an optical pyrometer, calibrated against the melting point of Na_3PO_4 (1583°C) and $Ca_3(PO_4)_2$ (1810°C). Also freezing was used for phase determination. Samples that were brought about the equilibrium state (in the furnace with PtRh30 winding) were frozen in ice. Such freezing of samples from the horizontal furnaces was not possible, because of their design (operation in argon).

X-ray diffraction was performed by a Siemens D 5000 diffractometer (CuK_α radiation, Ni filter, scintillating counter) and an HZG-4 diffractometer (Guinier camera, CuK_α radiation, Ni filter). In order to determine the lattice parameters a packet of PROSZKI [4] was employed. Lattice parameters were determined in two stages. At the first stage tentative values were determined by the indexing program DICVOL [5]. At the next stage the lattice parameters were evaluated more precise by the program APPLEMAN [6] (using the least squares method).

RESULTS AND DISCUSSION

Phase equilibria in the system $CePO_4$–$Ba_3(PO_4)_2$ were investigated in the whole range of composition and temperature by thermal analysis (including also differential thermal analysis of heating and cooling) and powder X-ray diffraction.

At first, an investigation was carried out to check whether in the $CePO_4$–$Ba_3(PO_4)_2$ system an intermediate compound $Ba_3Ce(PO_4)_3$ would appear, as expected from literature, as well as an equivalent of the phosphate $Ba_7Ce(PO_4)_6$. The orthophosphate $Ba_3Ce(PO_4)_3$ appears with a molar ratio $CePO_4$:$Ba_3(PO_4)_2$ of 1:1 (71.91 wt % $Ba_3(PO_4)_2$, 28.09 wt % $CePO_4$). A stoichiometric mixture of the initial orthophosphates was prepared, thoroughly mixed and rubbed to be finally formed into pellets, which were placed in platinum crucibles and heated at different temperatures, *i.e.* 1350, 1450, 1550 and 1650°C for 30 min, which was followed by a slowly cooling to room temperature. The phase composition of the sinters obtained was checked in each case by X-ray diffraction. It was found that the samples after heating at 1350°C had a diphase character: diffraction patterns showed reflections originated from the initial orthophosphates. In contrast, the sinters of 1450, 1550 and 1650°C were single phases and had an eulytite structure. This means that the existence of the double orthophosphate $Ba_3Ce(PO_4)_3$ together with its eulytite structure, and its occurrence in the $CePO_4$–$Ba_3(PO_4)_2$ system as an intermediate compound, was confirmed. The lattice parameter *a* of this compound was determined as 10.498 Å, which coincides with that of [1]. It is found that $Ba_3Ce(PO_4)_3$ melts congruently at about 2080°C and is stable down to room temperature. DTA curves (both of heating and cooling) below 1450°C do not reveal any thermal effects, what indicates that this compound is not involved in a polymorphic transformation between 1450–20°C.

To determine initially the phase equilibria in the subsolidus region of the $CePO_4$–$Ba_3(PO_4)_2$ system, phase X-ray analysis was employed. It was found in the composition range of $CePO_4$–$Ba_3Ce(PO_4)_3$ that a perfect mutual insolubility of phases occurred. Indeed, diffraction patterns of the presynthesized samples revealed only reflections typical of $CePO_4$ and $Ba_3Ce(PO_4)_3$. Interpretation of diffraction patterns of the sinters of the composition range of $Ba_3Ce(PO_4)_3$–$Ba_3(PO_4)_2$ appeared rather not to be unequivocal. Consequently, it was necessary to examine in detail this composition range (*i.e.* in the barium orthophosphate $Ba_3(PO_4)_2$-rich part of the system). In addition, another reason for undertaking the examination was information about the existence of the double orthophosphate $Ba_7Ce(PO_4)_6$ [2]. This compound appears with a molar ratio $Ce^{IV}_3(PO_4)_4 : Ba_3(PO_4)_2$ equal to 1:7 (15.96 wt% $Ce^{IV}_3(PO_4)_4$ and 84.04 wt % $Ba_3(PO_4)_2$). Hence, it was reasonable to suppose that in the $Ba_3(PO_4)_2$-rich part of the $CePO_4$–$Ba_3(PO_4)_2$ system a compound would be formed as an equivalent compound of $Ba_7Ce(PO_4)_6$ orthophosphate.

At the first stage of investigation heteromolar mixtures of the parent orthophosphates, with the compositions $Ba_3(PO_4)_2:CePO_4 > 1$ (*i.e.* $Ba_3(PO_4)_2:CePO_4 >$ 71.91 wt % $Ba_3(PO_4)_2$) were sintered between 1450–1650°C for 0.5 h, and then slowly cooled down to room temperature. Freezing the samples was also employed, starting from the temperature of the heating. Based on the phase X-ray analysis of the above sinters it was established what follows: 1) diffraction patterns of the samples within the composition range 71.91–83.66 wt % $Ba_3(PO_4)_2$, after thermal treatment, showed only reflections originated from a phase of eulytite structure; 2) samples containing more than 83.66 wt % $Ba_3(PO_4)_2$, after thermal treatment, represented a two-phase mixture, *i.e.* the orthophosphate $Ba_3(PO_4)_2$ and a phase of eulytite structure.

In view of the results obtained, it was necessary to observe the change in lattice parameter *a* of the $Ba_3Ce(PO_4)_3$ orthophosphate, both at room temperature and a high temperature (1450°C). Two series of samples were prepared for this purpose. Samples of one series were presynthesized *via* heating at 1450°C for 0.5 h, and slowly (5°/min) cooled down to room temperature. In the other series samples were presynthesized, cooled to room temperature, carefully rubbed and anew heated at 1450°C for 0.5 h, after which they were quenched. Powder X-ray diffraction based values of the lattice parameter *a* for selected samples of both series (in the composition range 60–90 wt % $Ba_3(PO_4)_2$) are collected in Table 1. The course of variation of the constant *a* is graphically shown in Fig. 1. Almost the same value of the lattice parameter *a* for the samples No. (1) and (2) confirms our earlier results showing that, in the $CePO_4$-rich part of the system, a perfect mutual insolubility of phases occurs. For the samples denoted (3), (4) and (5) an insignificant, but systematic, rise in the parameter *a* is observed. This indicates the existence of solid solutions in the composition range 71.91–83.66 wt % $Ba_3(PO_4)_2$. Sample (5) has a composition of 83.66 wt% $Ba_3(PO_4)_2$, 16.34 wt % $CePO_4$. This composition is depicted by a molar ratio of $CePO_4$: $Ba_3(PO_4)_2 = 1:2$ and the formula $Ba_6Ce(PO_4)_5$. The sample with the composition $Ba_6Ce(PO_4)_5$, like the orthophosphate $Ba_3Ce(PO_4)_3$, has eulytite structure. For samples (5) and (6) the value of parameter *a* almost does not change, which suggests that a perfect mutual insolubility of phases occurs in the $Ba_3(PO_4)_2$-richest part of the system $CePO_4$–$Ba_3(PO_4)_2$.

Table 1. Values of lattice constant a of the orthophosphate $Ba_3Ce(PO_4)_3$ in the composition range 60–90 wt % $Ba_3(PO_4)_2$, at temperatures 25°C and 1450°C.

No. of sample *(vidi Fig. 1)*	wt % $(Ba_3PO_4)_2$	Lattice constant *a* [Å] at 25°C	Standard deviation	Lattice constant *a* [Å] at 1450°C	Standard deviation
1	60	10.4991	0.0003	10.4988	0.0005
2	71.91[$Ba_3Ce(PO_4)_3$]	10.4986	0.0006	10.4969	0.0008
3	75	10.5158	0.0005	10.5141	0.0005
4	80	10.5347	0.0004	10.5314	0.0008
5	83.66	10.5514	0.0004	10.5474	0.0006
6	90	10.5482	0.0012	10.5468	0.0015

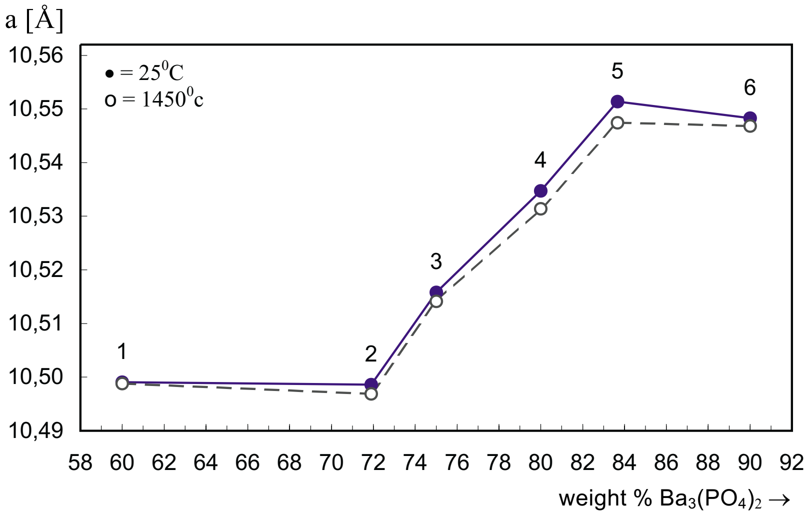

Figure 1. Variation of the lattice constant a of the orthophosphate $Ba_3Ce(PO_4)_3$ in the composition range 60–90 wt % $Ba_3(PO_4)_2$, at temperature 25°C and 1450°C.

It was not possible, because of apparatus limitations, to determine unequivocally whether (i) in the composition range 71.91–83.66 wt % $Ba_3(PO_4)_2$ either continuous or limited solid solutions occur and (ii) the formula $Ba_6Ce(PO_4)_5$ either can be ascribed to a new, double barium and cerium (III) orthophosphate or rather it corresponds to a maximum solubility of $Ba_3(PO_4)_2$ in the eulytite structure $Ba_3Ce(PO_4)_3$.

It should be stressed, first of all, that samples of the system $CePO_4$–$Ba_3(PO_4)_2$ melt at very high temperatures, well above 1600°C. For this reason, it was difficult to find the shape of liquidus curves, and especially the one of solidus curves. Likewise, phase dependences at above 1450°C for the composition range 71.91–83.66 wt % $Ba_3(PO_4)_2$ could not be unequivocally determined. Otherwise one should carry out a DTA and X-ray investigation at high temperatures – well above 1450°C.

Based on the results of thermal and X-ray investigations a phase diagram of the system $CePO_4$–$Ba_3(PO_4)_2$ has been proposed. It is presented in Fig. 2. Melting points of the samples were determined by an optical pyrometer and such values are approximate. Hence, the liquidus as well as solidus curves are drawn with dashed line. Two eutectics occur in the system. Their parameters are: eutectic e_1 has the composition 65 wt % $Ba_3(PO_4)_2$, 35 wt % $CePO_4$ and it melts at about 1840°C; eutectic e_2 has the composition 99 wt % $Ba_3(PO_4)_2$, 1 wt % $CePO_4$ and melts at about 1600°C. Orthophosphate $Ba_3(PO_4)_2$ appears in two polymorphic modifications. For the pure compound the

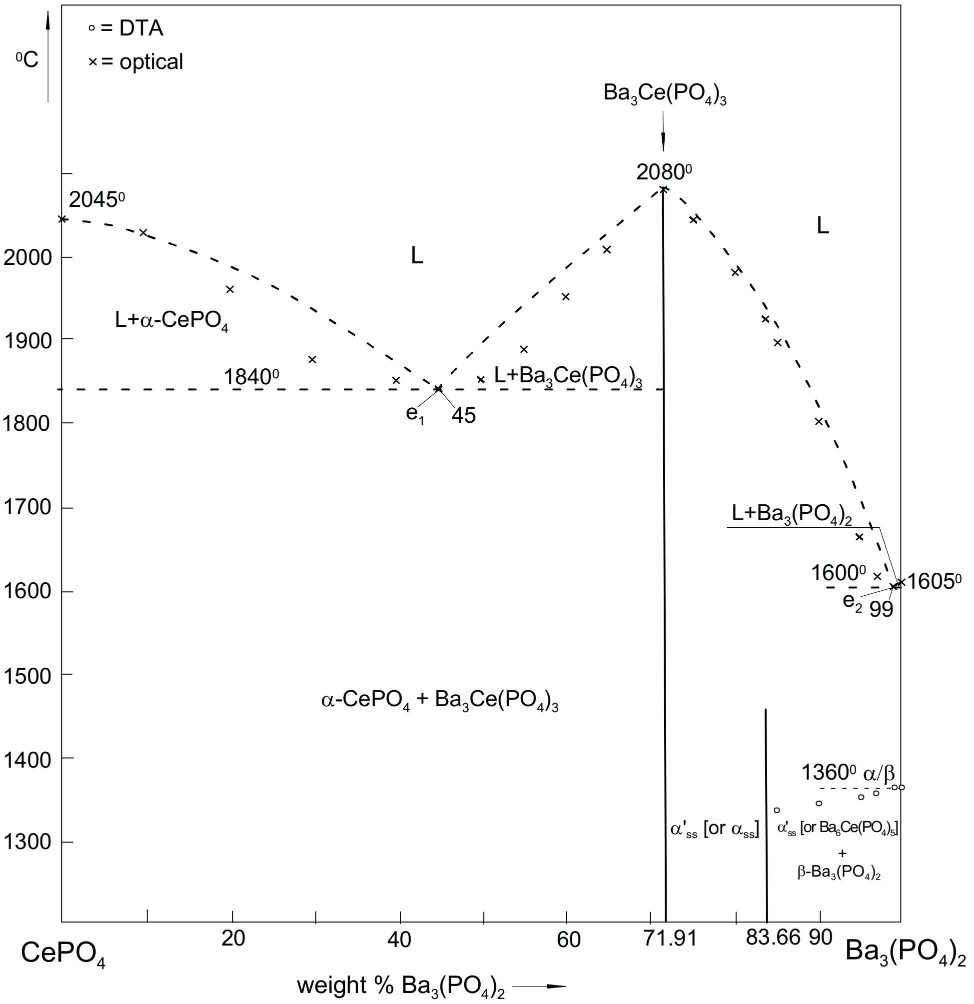

Figure 2. Phase equilibria in the system $CePO_4$–$Ba_3(PO_4)_2$.

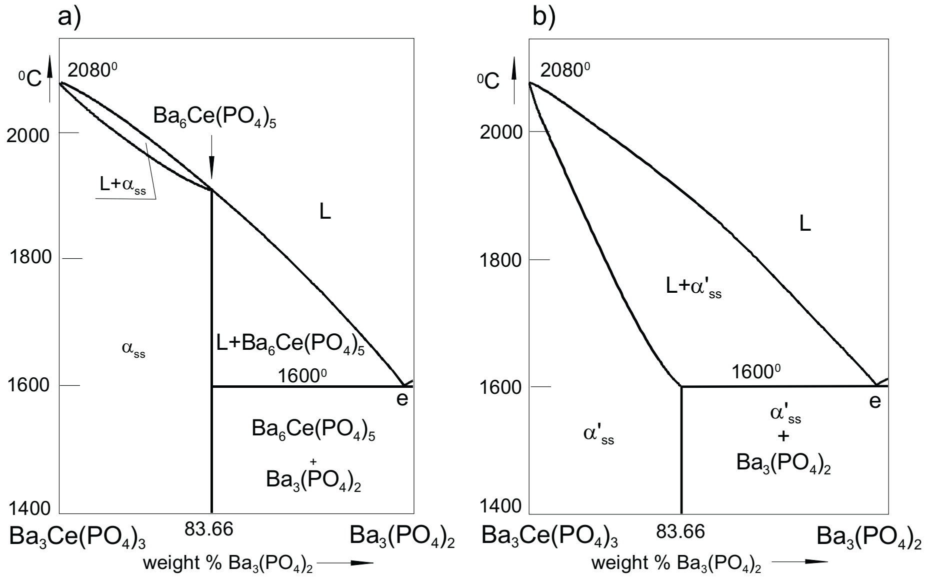

Figure 3. Hypothetic phase diagram (in a simplified form) of the system $CePO_4$–$Ba_3(PO_4)_2$ in the composition range 71.91–100 wt % $Ba_3(PO_4)_2$, at high temperatures, assuming alternatively: a) $Ba_6Ce(PO_4)_5$ to be a double barium-cerium(III) orthophosphate; (α_{ss} = continuous solid solution), b) the formula $Ba_6Ce(PO_4)_5$ to correspond to the maximum solubility of $Ba_3(PO_4)_2$ in the eulityte structure $Ba_3Ce(PO_4)_3$; (α'_{ss} = limited solid solution).

transition α/β proceeds at 1360°C. In the system this transition is observed at lower temperatures. Likewise, orthophosphate $CePO_4$ appears in two polymorphic modifications. Their transition point is at 620°C [7]. However, DTA curves of the samples of the $CePO_4$–$Ba_3(PO_4)_2$ system did not show any thermal effects connected to this transformation.

Fig. 3 shows (additionally) two possible variants of the occurrence of phase dependence in the composition range 71.9–100 wt % $Ba_3(PO_4)_2$ at high temperatures.

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