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PHASE EQUILIBRIUM IN THE SYSTEM LaP_3O_9–$NaPO_3$–P_2O_5 The new compounds $NH_4LaP_4O_{12}$ and $La_4(P_2O_7)_3$

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Abstract

The phase diagram of the ternary system LaP_3O_9–$NaPO_3$–P_2O_5 was constructed through the use of a new compound $NH_4LaP_4O_{12}$. Ammonium lanthanum phosphate $NH_4LaP_4O_{12}$ crystallizes in the monoclinic system, space group C2/c, with $a=7.941(4)$Å, $b=12.645(13)$Å, $c=10.702(9)$Å, $\gamma=110.00(5)$. The compound melts incongruently at 1198°C. Lanthanum pyrophosphate melts incongruently at 1160°C.

Keywords: $NH_4LaP_4O_{12}$, $La_4(P_2O_7)_3$, phase diagram, system LaP_3O_9–$NaPO_3$–P_2O_5

Introduction

The purpose of the present paper is to report the phase diagram of the unknown system LaP_3O_9–$NaPO_3$–P_2O_5. It is limited by the following binary systems: LaP_3O_9–LaP_5O_{14}; LaP_5O_{14}–P_2O_5; P_2O_5–$NaPO_3$; and $NaPO_3$–LaP_3O_9. The phase diagram for the binary system $NaPO_3$–LaP_3O_9 with the compound $NaLaP_4O_{12}$ is known [5, 7–9]. Data on the fusion temperatures and structures of the metaphosphates $Ln(PO_3)_3$ and LaP_5O_{14} are restricted to [7, 10–13]. The solid phases in the equilibrium system NaO_2–P_2O_5–H_2O have been reported [14]. Tananaev *et al.* [15–18] reported on the diphosphates $P_2O_7^{4-}$: $Ln^{3+}=0.5{:}0.6$ and $Ln_4(P_2O_7)_3xH_2O$, where Ln=La, Gd, Sm and Y.

Experimental

The following starting materials were used: $NaPO_3$, sodium metaphosphate (POCH), and a new ammonium lanthanum polyphosphate, $NH_4LaP_4O_{12}$, which was obtained by the following method [1].

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$NH_4H_2PO_4$, ammonium hydrophosphate (POCH), La_2O_3 (99.99%) and $NaLaO_2$ were mixed together and ground in an agate mortar in the mass ratio 7:1. 5:0. 87 and then heated in the interval 180–220°C for 20 min. In the second step, the mixture was heated to 700°C at a rate of 10 deg·min^{-1}. Queinching in air led to ammonium lanthanum polyphosphate with the formula $NH_4LaP_4O_{12}$, which was washed with water.

Powder LaP_4O_9 was obtained from crystals of $NH_4LaP_4O_{12}$ which were heated in the interval 700–1000°C for 0.5 h.

$$NH_4LaP_4O_{12} + NH_4H_2PO_4 \xrightarrow{\text{heat}} 2NH_3 + 2H_2O + P_2O_5 + LaP_3O_9$$

LaP_5O_{14} was also used as a starting material. Ultraphosphate LaP_5O_{14} was synthetized by the solid-state reaction from lanthanum metaphosphate, LaP_3O_9, and $NH_4H_2PO_4$ (POCH):

$$LaP_3O_9 + 2\ NH_4H_2PO_4 = LaP_5O_{14} + 2\ NH_3 + 3\ H_2O$$

Samples in the binary system and the ternary system were synthetized from $NaLaP_4O_{12}$, LaP_3O_9, LaP_5O_{14}, $NaPO_3$ and $NH_4H_2PO_4$ in open platinum and gold crucibles.

Temperature was measured with a Pt/PtRh 10 thermocouple. In thermal studies involving heating, a MOM 3427 derivatograph was used with photographic recording over the temperature range from 20 to 1300°C.

The operating conditions used were as follows: sensitivity 150 mg, heating rate 7.5 deg·min^{-1}. Al_2O_3 was used as a standard material. In the thermal studies involving cooling, an LP 839 temperature programmer (Chinoin, Budapest) was used.

Infrared absorption data were obtained with a Perkin-Elmer instrument (University of Wrocław). The samples were pressed in KBr pellets and mixed in a Nujol suspension. Unit cell parameters for $NH_4LaP_4O_{12}$ were determined from Syntex $P2_1$ (University of Wrocław).

Results and discussion

Single-crystal X-ray analysis proved that the compound is $NH_4LaP_4O_{12}$, which is stable at elevated temperatures. Preliminary X-ray data are: system monoclinic, space group C2/c, with a=7.941(4) Å; b=12.645(13) Å; c= 10.702(9) Å; γ=110.00(5).

Diffractometer-collected data were reduced in a standard way, the absorption correction being allowed for by using the program DIFABS. The refinement led to R_1=3.7 and R_2=4.6%. The structure consists of PO_4 tetrahedra linked to form tetracycles, LaO_8 dodecahedra and NH_4^+ tetrahedra octahedrally sur-

rounded by O atoms. The La–O bond lengths varybetween 2.473(6) and 2.520(5) Å, the dodecahedron resembling that found in LaP_3O_9 [2, 3]. The crystals are isomorphous with those of $NH_4PrP_4O_{12}$ [4] and unpublished data of Matuszewski and Kropiwnicka.

$NH_4LaP_4O_{12}$ melts incongruently at 1198°C with a peritectic reaction at 848°C. From the crystals, ammonium lanthanum phosphate and lanthanum metaphosphate were obtained in 100% yield. The purity of the compound was checked by means of X-ray and IR spectroscopy. LaP_3O_9 had the following unit cell parameters: $a=11.27$ Å; $b=8.60$ Å and $c=7.36$ Å [2, 3].

Phase diagram of the binary system LaP_5O_{14}–$NaPO_3$

The phase diagram of the system LaP_5O_{14}–$NaPO_3$ is presented Fig. 1. The thermal points were obtained via thermal (heating and cooling) analyses and microscopic, X-ray and visual analyses (Technological Institute of Chemical and Food Industry). Samples from this system form glazes, decompose quite easily and are very hygroscopic. The phase diagram of sodium metaphosphate and lanthanum ultraphospate has a eutectic character. The eutectic occurs at 25 wt% LaP_5O_{14} and 75 wt% $NaPO_3$ at 520°C. The polymorphic transformations α/β and β/γ-$NaPO_3$ occurred throughout the composition range as strong thermal effects in the heating curves. The experiment was carried out with monocrystals of LaP_5O_{14}.

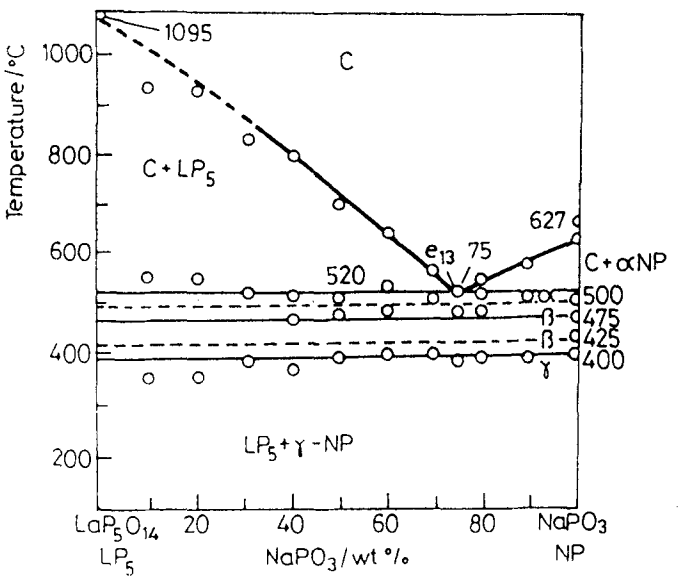

Fig. 1 Phase diagram of the system LaP_5O_{14}–$NaPO_3$

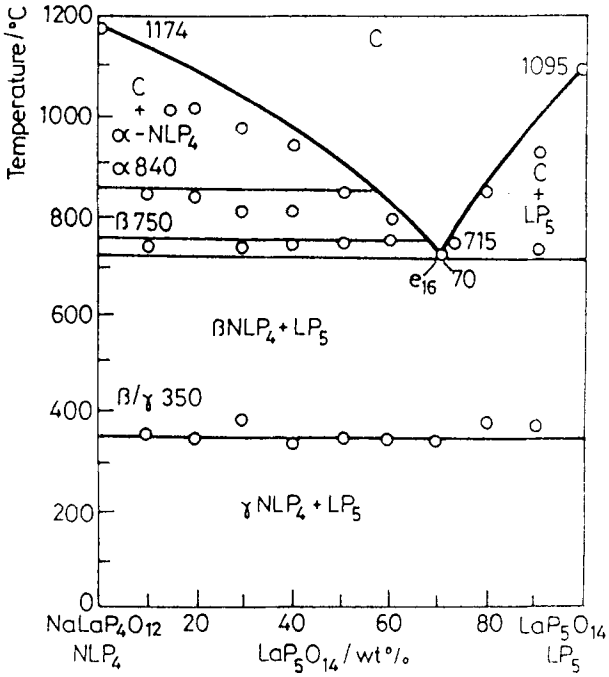

Fig. 2 Phase diagram of the system $NaLaP_4O_{12}$–LaP_5O_{14}

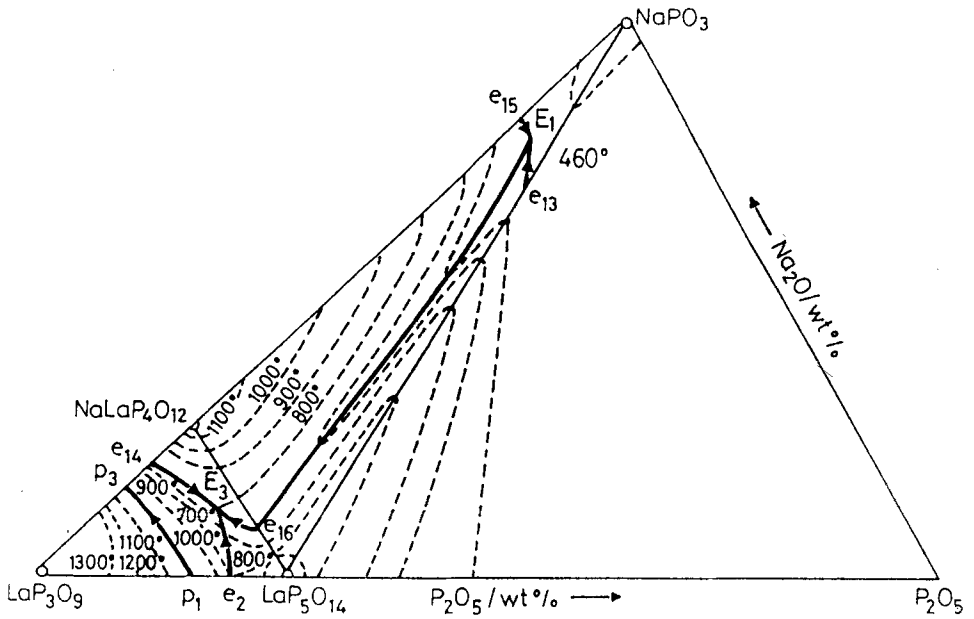

Fig. 3 Phase diagram of the ternary system LaP_3O_9–$NaPO_3$–P_2O_5

Phase diagram of the binary system $NaLaP_4O_{12}$–LaP_5O_{14}

Figure 2 presents the phase diagram of the system $NaLaP_4O_{12}$–LaP_5O_{14}, which was obtained from thermal and X-ray analyses using monocrystals of $NaLaP_4O_{12}$ and LaP_5O_{14} according to the methods described in [6]. The monocrystals of $NaLaP_4O_{12}$ were obtained as the low-temperature γ-$NaLaP_4O_{12}$ form [5]. The eutectic consists of 30 wt% $NaLaP_4O_{12}$ and 70 wt% LaP_5O_{14} at 715°C. The system was very difficult to work with because of the crystallization of all samples as glazes. The samples rich in LaP_5O_{14} decomposed very easily into P_2O_5 and La_2O_3 at high temperatures.

The polymorphic transformations α/β-$NaLaP_4O_{12}$ (820–750°C) and β/γ-$NaLaP_4O_{12}$ (350°C) occurred throughout the composition range. The thermal effects for α/β-$NaLaP_4O_{12}$ (820–750°C) corresponded with the thermal effect from the eutectic.

The discussed binary systems divide the studied partial system LaP_3O_9–$NaPO_3$–P_2O_5 into the following three partial ternary systems:

1. LaP_3O_9–$NaLaP_4O_{12}$–LaP_5O_{14}
2. LaP_5O_{14}–$NaLaP_4O_{12}$–LaP_5O_{14}
3. LaP_5O_{14}–$NaPO_3$–P_2O_5

In the ternary system LaP_3O_9–$NaLaP_4O_{12}$–LaP_5O_{14}, the ternary eutectic 32 wt% La_2O_3, 3.8 wt% Na_2O, 63.8 wt% P_2O_5 crystallizes at 700°C, with four yields of the first crystallization:

1. e_2E_3–$NaLaP_4O_{12}$ + LaP_5O_{14}
2. $e_{16}E_2$–LaP_3O_9 + $NaLaP_4O_{12}$
3. $e_{14}E_3$–LaP_3O_9 + LaP_5O_{14}
4. p_1p_3, where we deal with the binary peritectic reaction $c_{p_1p_3}$ + $LaPO_4$ = LaP_3O_9.

The ternary system $NaLaP_4O_{12}$–$NaPO_3$–LaP_5O_{14}

In the ternary system $NaLaP_4O_{12}$–$NaPO_3$–LaP_5O_{14}, samples were insoluble together in the solid state and formed a ternary simple eutectic at 460°C with the composition 4 wt% La_2O_3, 24 wt% Na_2O, 72 wt% P_2O_5.

The ternary samples in the ternary system LaP_5O_{14}–$NaPO_3$–P_2O_5 were synthetized from $NaPO_3$, monocrystals of LaP_5O_{14} and $NH_4H_2PO_4$ in open crucibles in two steps:

1. at 180°C for from 10 to 20 min.
2. at 300°C for from 25 to 40 min.

In the thermal studies, the thermal effects were observed during heating. The effects were used to construct the isotherms in the phase diagram for LaP_3O_9–$NaPO_3$–P_2O_5. The ultraphosphate LaP_5O_{14} and P_2O_5 form a simple eutectic e_1 with the composition 84 wt% P_2O_5 and 16 wt% La_2O_3 at 220°C.

Synthesis of $La_4(P_2O_7)_3$

0.0867 g $NaLaO_2$ was mixed with 0.1357 g La_2O_3 (USSR) and 0.6750 $NH_4H_2PO_4$. The sample was heated in a gold crucible in a kantal furnace at 180°C for 15 min. The molar ratio was 5:1:0.6.

Next, the mixture was heated to 700°C at a rate of 5 deg·min^{-1} and quenched in air. Crystalline $NH_4LaP_4O_{12}$ was obtained and washed with water. The compound $NH_4LaP_4O_{12}$ forms a hydrate of formula $NH_4LaP_4O_{12}\cdot H_2O$. Loss of the water occurs at 478°C, and the loss in weight is 1.33%.

Crystalline ammonium lanthanum polyphosphate was heated slowly in a gold crucible under pressure to 280°C for 5 h:

$$4NH_4LaP_4O_{12} \xrightarrow[\text{pressure}]{280^\circ C} 4NH_3 + 2.5P_4O_{10} + 2H_2O + La_4(P_2O_7)_3 =$$

$$\xrightarrow[\text{open}]{700^\circ C} 4LaP_3O_9 + 4NH_3 + 2H_2O + 2P_2O_5.$$

The compound was assigned the following formula: $La_4(P_2O_7)_3$. The purity of the phosphate was checked by IR spectroscopy. The IR spectrum was measured in KBr pellets and Nujol suspension (University of Wrocław) for $La_4(P_2O_7)_3$ and shows clear bands for the valence frequencies of the pyrophosphate group $P_2O_7^{4-}$ at 735 cm^{-1} *vs.* (P–O–P) [19].

The pyrophosphate melts incongruently at 1160°C and appears in one polymorphic form (Enterprise of the Cooling Industry, Wrocław).

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Zusammenfassung — Unter Einsatz der neuen Verbindung $NH_4LaP_4O_{12}$ wurde das Phasendiagramm des ternären Systemes LaP_3O_9–$NaPO_3$–P_2O_5 erstellt. Das Ammoniumlanthanphosphat $NH_4LaP_4O_{12}$ kristallisiert im monoklinen System, Raumgruppe C2/c mit $a=7.941(4)$Å, $b=12.645(13)$Å, $c=10.702(9)$Å, $\gamma=110.00(5)$. Die Verbindung schmilzt inkongruent bei 1198°C. Lanthanpyrophosphat schmilzt inkongruent bei 1160°C.