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PHASE EQUILIBRIA IN THE SYSTEM La_2O_3-Na_2O-P_2O_5
The partial system La_2O_3-$Na_4La_2P_4O_{15}$-$LaPO_4$

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In the ternary system La_2O_3-P_2O_5-Na_2O the partial system La_2O_3-$Na_4La_2P_4O_{15}$-$LaPO_4$ has been examined by the thermal, dilatometric X-ray and microscopic analyses and its phase diagram provided. The lanthanum oxyphosphate La_3PO_7 melts incongruently at the 1590°C temperature and crystallizes in a monoclinic system a = 11.20 Å, b = 11.94 Å, c = 7.01 Å, γ = 93.79 and V = 936.97 Å^3.

The purpose of present paper is to determine the phase diagram of the partial system La_2O_3-$Na_4La_2P_4O_{15}$-$LaPO_4$. As yet this system has not been known. It is limited from three sides by the following binary system: La_2O_3-$LaPO_4$–; La_2O_3-$Na_4La_2P_4O_{15}$; $LaPO_4$-$Na_4La_2P_4O_{15}$. The oxyphosphate with a formula La_3PO_7 for the first time has been obtained by Serra J. J. [1], in a solid state reaction from $NH_4H_2PO_4$ and La_2O_3 at 1180°, and by chemical decomposition of the orthophosphate $LaPO_4$ at a high temperature in an atmospheric pressure conditions [2]. Serra *et al.* [1] reported that the structures of La_3PO_7 and $La_7P_3O_{18}$ are monoclinic and $La_7P_3O_{18}$ exists in low - and high - temperature forms, transforming reversibley at 1650°. Kizilyalli and Welch made La_3PO_7 by solid state reaction of $LaPO_4$ with Na_2CO_3 at 700° to 900° [3]. Lanthanum oxyphosphate La_3PO_7 was found by quenching studies to have a slogish inversion at 935° [4]. The oxyphosphate La_3PO_7 melts incongruently at 1590° temperature [5, 6].

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Experimental

The following initial materials were used for the synthesis of lanthanum phosphates and sodium - lanthanum phosphates: lanthanum oxide - 99.99 % (USSR), monobasic ammonium phosphate $NH_4H_2PO_4$ analytical grade (POCH), monobasic sodium phosphate $NaH_2PO_4.H_2O$ analytical grade (POCH). The samples of ternary system La_2O_3-$Na_4La_2P_4O_{15}$-$LaPO_4$ were synthetized in the solid phase by sintering the mixtures of initial components at 600^o-1200^o for 6-8 hours. The oxyphosphate La_3PO_7 was obtained in a solid state reaction from a new compound $NH_4LaP_4O_{12}$ [7], by the heating at the high - temperature $NH_4LaP_4O_{12}$, and from $NH_4H_2PO_4$ (anal. grade), La_2O_3 99.99 % (USSR) by the following reaction:

$$NH_4LaP_4O_{12} + NH_4H_2PO_4 + La_2O_3 = La_3PO_7 + 2NH_3 + 2H_2O + 2P_2O_5$$

The reaction proceeds in two stages:
1. at 400^o temperature for 6 hours
2. at 1400^o temperature for 8 hours

in a platinum crucible. Synthesis of sodium - lanthanum phosphates: $Na_4La_2P_4O_{15}$ and $Na_3La_2(PO_4)_3$ were carried out in the manner given in [8].

In thermal studies during a heating the Paulik-Paulik-Erdey MOM 3427 derivatograph was used with photographic recording over the temperature range from 25 to 1300^o. Operating conditions were used as follows: sensitivity TG - 500 mg, DTA-1/5, DTG 1/10 heating rate 10 deg/min. Al_2O_3 was used as a standard material. High-temperature X-ray GPWT-1500 attachment installed in a GUR-5 goniometer of a DRON-2.0 diffractometer [9].

Results and discussion

Side system $LaPO_4$-$Na_4La_2P_4O_{15}$

The unknown side system $LaPO_4$-$Na_4La_2P_4O_{15}$ limiting the partial system La_2O_3-$Na_4La_2P_4O_{15}$-$LaPO_4$ from one side, was studied by the methods of thermal analyses of heating and cooling the previously melted samples as well as by microscopic and X-ray analyses over the composition range from 20 to 100 weight % of $Na_4La_2P_4O_{15}$.

Figure 1 presents the phase diagram of the discussed binary system. The initial phosphates form a simple eutectic system. The e_{19} eutectic appears at

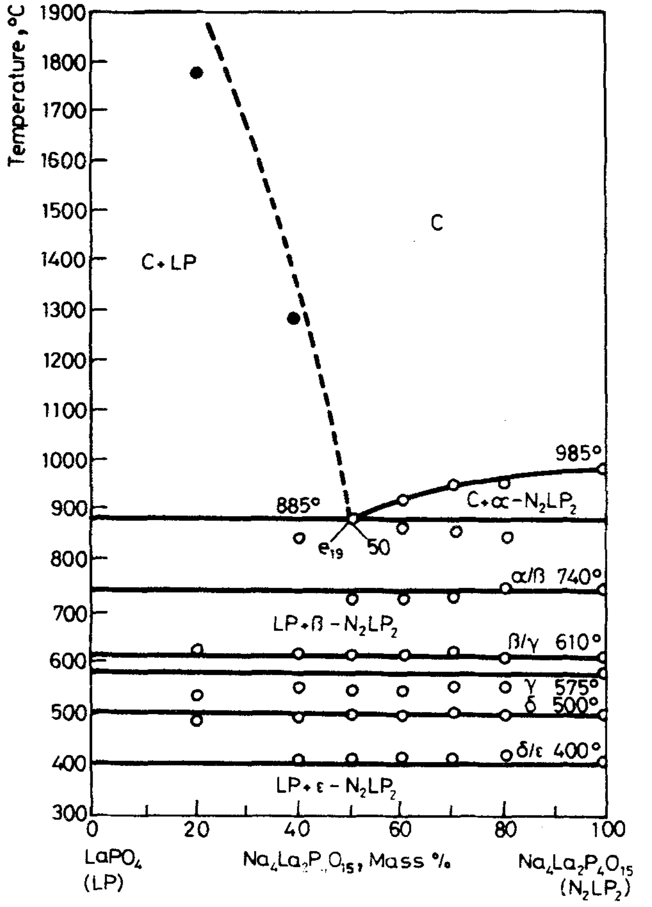

Fig. 1 Phase diagram of $LaPO_4$ - $Na_4La_2P_4O_{15}$ system. o - thermal analysis, • - optical

50 weight % of $LaPO_4$ and 50 weight % of $Na_4La_2P_4O_{15}$ and at temperature 885°. Polymorphic transitions α/β- at 740° and δ/ε - $Na_4La_2P_4O_{15}$ at 400° give thermal effects merely in that part of the system which is richer in this phosphate. Whereas thermal effects due to the transitions β/γ - at 610° and γ/δ, occurring at temperatures interval 575-500°, give distinct thermal effects over the entire composition being studied. The samples from the discussed system are very hygroscopic. Their microscopic studies were made difficult.

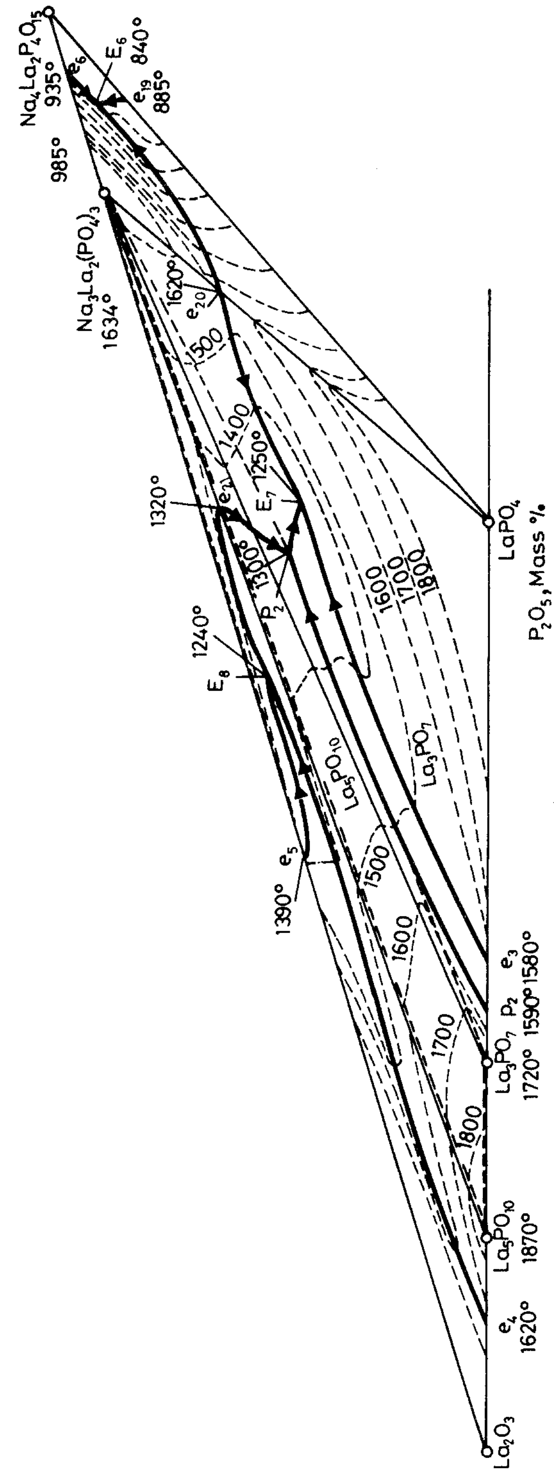

Fig. 2 Phase diagram of La_2O_3 - $Na_4La_2P_4O_{15}$ - $LaPO_4$ system

Partial ternary system La_2O_3-$Na_4La_2P_4O_{15}$-$LaPO_4$

Figure 2 presents the phase diagram of partial ternary system La_2O_3-$Na_4La_2P_4O_{15}$-$LaPO_4$ with solidifications isotherms. Three hitherto unknown binary sections: 1/ La_5PO_{10}-$Na_3La_3(PO_4)_3$, 2/ La_3PO_7-$Na_3La_2(PO_4)_3$ and 3/ $LaPO_4$-$Na_3La_2(PO_4)_3$ occur in the composition range under investigation. Figure 3 presents the phase diagram of binary section La_5PO_{10}-$Na_3La_2(PO_4)_3$ obtained by thermal analysis of cooling and heating, dilatometric and X-ray analyses.

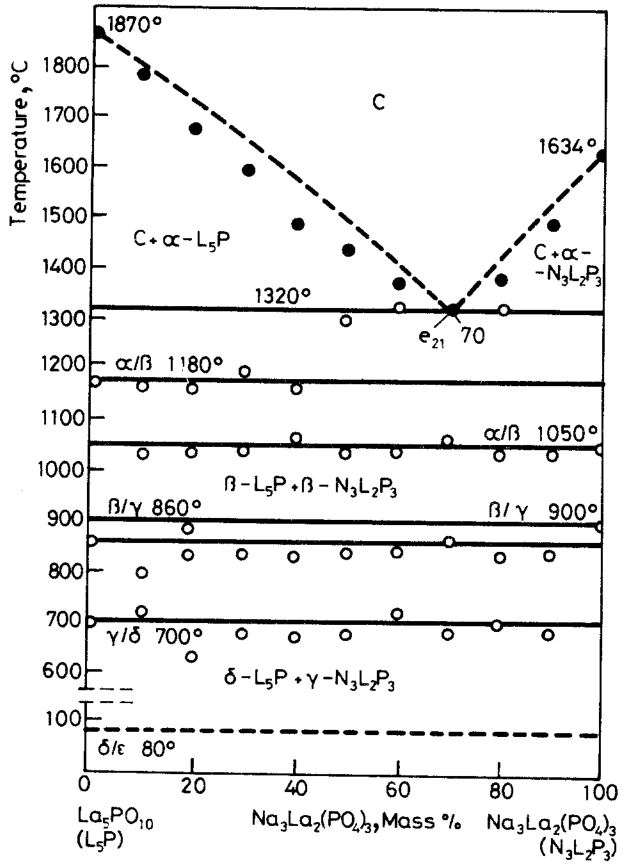

Fig. 3 Phase diagram of La_5PO_{10} - $Na_3La_2(PO_4)_3$ system. o - thermal analysis, • - optical

This is a simple eutectic system. The eutectic temperature is 1320°, composition e_{21}: 70 weight % of $Na_3La_2(PO_4)_3$, 30 weight % of La_5PO_{10}.

Microphotograph of the sample of discussed binary system composed: 70 weight % of La_5PO_{10} and 30 weight % of $Na_3La_2(PO_4)_3$ is presented in Fig. 4. The primarily separated crystals La_5PO_{10} and the eutectic (dark fields) are seen.

Fig. 4 Composition: 70% La_5PO_{10} 30% $Na_3La_2(PO_4)_3$. Preliminary: La_5PO_{10} (white crystals). Secondarily: eutectic (dark fields)

The samples for phase studies were obtained by sintering the initial components at 1000° and further by melting in a furnace with the tungsten winding. The liquidus curve was determined by optical pyrometer. The dependences in solid phase were based on thermal analysis of cooling the previously melted samples.

Polymorphic transitions α/β - La_5PO_{10} at 1180° gives separate thermal effects over the composition range from 60 to 100 weight % of La_5PO_{10}. In the remaining range of compositions these effects coincide with these coming from high-temperature transitions α/β - $Na_3La_2(PO_4)_3$ at 1050° giving a strong common thermal effect over the entire composition range. The transitions β/γ-La_5PO_{10} at 860° and β/γ-$Na_3La_2(PO_4)_3$ at 900° give a strong common thermal effect. The transition γ/δ-La_5PO_{10} at 700° is characterized by a strong thermal effects over the entire composition range. The transition δ/ε-La_5PO_{10} at 80° was observed in dilatometric studies. The samples melted from system La_5PO_{10}-$Na_3La_2(PO_4)_3$ are not moisture resistant due to the hygroscopicity of the initial phosphates.

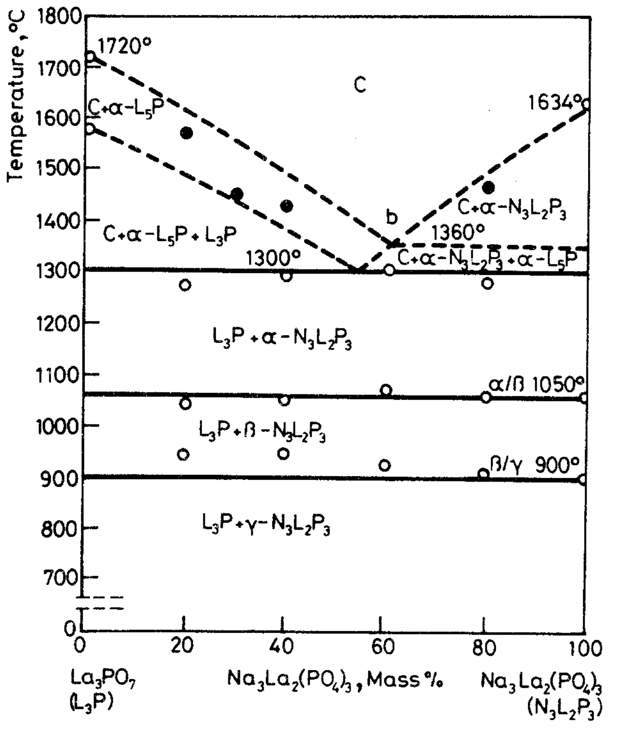

Fig. 5 Phase diagram of La_3PO_7 - $Na_3La_2(PO_4)_3$ system. o - thermal analysis, ● - optical

Figure 5 presents the phase diagram of binary section La_3PO_7-$Na_3La_2(PO_4)_3$. The system was studied by thermal analysis of heating the previously melted samples as well as by microscopic and X-ray analyses. The samples primarily synthetized from the initial components by sintering at 1000^0 were melted in a furnace with the tungsten winding. The liquidus curve was determined by optical pyrometer. The section La_3PO_7-$Na_3La_2(PO_4)_3$ though being limited by pure compounds does not possess all the features of a binary system. In its upper part has a ternary character. Above 1300^0 there occur the following four phases: liquid C, α-La_5PO_{10}, La_3PO_7 and α-$Na_3La_2(PO_4)_3$. As a result of the peritectic reaction: C + La_5PO_{10} $\rightarrow La_3PO_7$ the liquid C and the compound La_5PO_{10} become used up to yield La_3PO_7 crystals. Below 1300^0 there exist only two phases: La_3PO_7 and $Na_3La_2(PO_4)_3$. Polymorphic transitions α/β-$Na_3La_2(PO_4)_3$ at

1050° and β/γ at 900° give large thermal effect observed on heating curves over the entire binary system.

Microscopic analyses of microsections is difficult because of the hydroscopicity of initial phosphates.

The binary section $LaPO_4$-$Na_3La_2(PO_4)_3$ was studied over the composition range from 40 to 100 weight % of $Na_3La_2(PO_4)_3$ and over the temperature range from 20° to 1780°, to this end thermal analysis of heating and cooling the melted samples and X-ray and microscopic methods were used. The samples preliminary synthetized from the initial components by sintering at 1000° were melted in furnace with the tungsten winding. The liquidus curve was determined by optical pyrometer. Figure 6 presents the phase diagram of the discussed section.

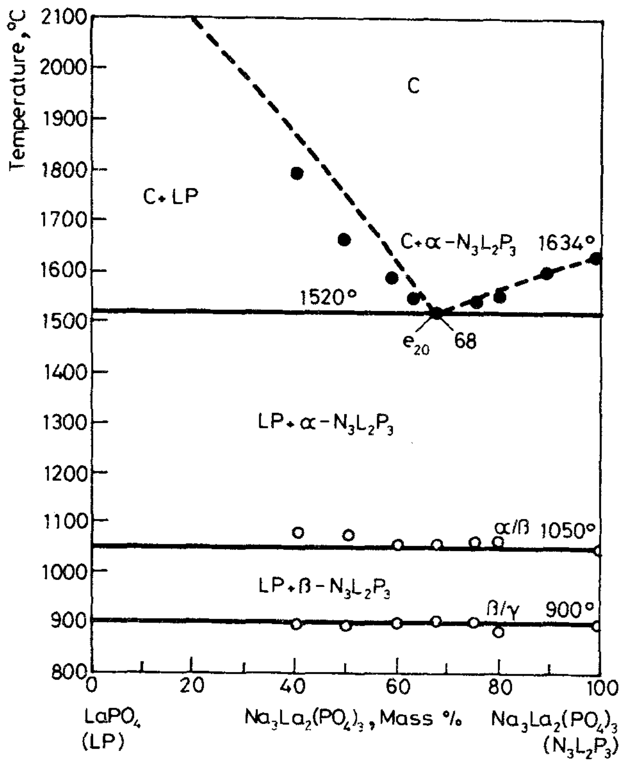

Fig. 6 Phase diagram of $LaPO_4$ - $Na_3La_2(PO_4)_3$ system. o - thermal analysis, • - optical

It is a simple eutectic system of eutectic composition e_{20}: 68 weight % of $Na_3La_2(PO_4)_3$ and 32 weight % of $LaPO_4$ and the temperature at 1520°. Polymorphic transitions α/β at 1050 ° and β/γ-$Na_3La_2(PO_4)_3$ at 900° give single distinct thermal effect over the entire composition range being examined.

The discussed binary sections divide the studied partial system La_2O_3-$Na_4La_2P_4O_{15}$–$LaPO_4$ into the next four partial ternary systems: 1/ La_2O_3–$Na_3La_2(PO_4)_3$–La_5PO_{10}, 2/ La_5PO_{10}–$Na_3La_2(PO_4)_3$–La_3PO_7, 3/La_3PO_7–$Na_3La_2(PO_4)_3$–$LaPO_4$ and 4/ $LaPO_4$–$Na_3La_2(PO_4)_3$–$Na_4La_2P_4O_{15}$. Within the studied range of compositions there occur four binary compounds (La_2O_3, La_5PO_{10}, La_3PO_7, $LaPO_4$) as well as two ternary compounds ($Na_3La_2(PO_4)_3$, $Na_4La_2P_4O_{15}$) which crystallize from the liquid phase.

In the binary system La_2O_3-$LaPO_4$ at the temperature of 1590° there occurs a peritectic reaction: C + α-La_5PO_{10} = La_3PO_7 which yields lanthanum oxyphosphate La_3PO_7. Hence during solidification of the samples corresponding to the field points La_5PO_{10}-La_3PO_7-P_2-$Na_3La_2(PO_4)_3$ (triple peritectic quadrangle) we deal with triple peritectic reaction: C_{P_2} + La_5PO_{10} = La_3PO_7 + $Na_3La_2(PO_4)_3$, where C_{P_2} means liquid of composition corresponding to P_2. The above reactions proceeds at constant temperature of 1300°. At this temperature in melted samples of La_3PO_7 - $Na_3La_2(PO_4)_3$ system there occur the equivalent amounts of the liquid of composition P_2 and α-La_5PO_{10} crystals. In the melted samples lying inside the triangle La_5PO_{10}-$Na_3La_2(PO_4)_3$-La_3PO_7 during peritectic reaction the liquid P_2 is depleted more quickly so that besides the formed La_3PO_7 and $Na_3La_2(PO_4)_3$ crystals there will remain an excess of La_5PO_{10} crystals. In the alloys lying inside the triangle La_3PO_7 - $Na_3La_2(PO_4)_3$ - P_2 peritectic reaction results in an excess of liquid C_{P_2} thus the solidification process is not finished in the peritectic temperature of 1300°. Further course of crystallization consists in crystallizing binary eutectic [La_3PO_7 + $Na_3La_2(PO_4)_3$] along the line P_2E_7 at varying temperatures and finally the point E_7 is reached starting crystallizing ternary eutectic {La_3PO_7 + $Na_3La_2(PO_4)_3$ + $LaPO_4$} at constant temperature 1250°.

Results and discussion of the diffraction data

The lanthanum oxyphosphate La_3PO_7 melts incongruently as a result peritectic reaction:

$$C + \alpha\text{-}La_5PO_{10} \rightarrow La_3PO_7$$

at the 1590° temperature and forms from a liquid phase C and a high temperature phase of the oxyphosphate α-La_5PO_{10}. The low-temperature phase of ε-La_5PO_{10} occurs in the monoclinic system and lattice parameters are following:

a = 13.11 Å; b = 13.58 Å; c = 8.08 Å; γ = 113.9; V = 1315.40 Å^3 [5, 6]

Powder diffraction data for the homogeneous phase La_3PO_7 are provided in Table 1.

Table 1 Lattice parameters for the low-temperature phase La_3PO_7

d_{exp}x10^{-1}nm	d_{cal}x10^{-1}nm	hkl
6.9757	7.0148	001
4.1556	4.1362	121
4.0402	4.0373	211
3.9637	3.9740	030
3.8251	3.8251	130
3.6333	3.6255	310
3.4624	3.4577	031
3.3647	3.3648	012
3.3558	3.3583	131
3.1280	3.1257	311
3.0217	3.0229	022
-	3.0192	221
2.9786	2.9805	040
2.9467	2.9431	122
2.5637	2.5606	240
2.5501	2.5540	302
2.4617	2.4649	331
2.3383	2.3382	003
-	2.3403	232
2.3094	2.3100	322
2.2540	2.2533	113
-	2.2559	340
2.2472	2.2479	142
-	2.2474	250
2.2013	2.2042	142
2.0037	2.0060	530
1.9256	1.9240	152
1.8590	1.8601	323
-	1.8596	610
1.8174	1.8127	620

Table 1 continued

d_{exp}x10^{-1}nm	d_{cal}x10^{-1}nm	hkl
1.8131	1.8125	451
1.7815	1.7836	352
1.7461	1.7457	020
1.7442	1.7467	361
1.7419	1.7413	532
1.7277	1.7266	243
-	1.7288	062
-	-	442
1.7205	1.7206	114
1.7187	1.7170	114
1.7127	1.7120	550
1.6878	1.6875	343
1.6774	1.6770	214
1.6626	1.6615	433
-	1.6612	153
-	1.6624	071
1.6568	1.6550	452
1.6541	1.6543	640

monoclinic system

a = 11.20 Å b = 11.94 Å c = 7.01 Å γ = 93.79 V = 936.97 Å^3

Powder data were obtained through use of the "Powder" program version IBM 360.

* * *

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Zusammenfassung — Mittels Thermo- und dilatometrischer Analyse, Röntgendiffraktionsuntersuchungen und Mikroskopie wurde das Teilsystem La_2O_3 - $Na_4La_2P_4O_{15}$ - $LaPO_4$ des ternären Systemes La_2O_3 - P_2O_5 - Na_2O untersucht und ein Phasendiagramm entwickelt. Lanthanoxyphosphat La_3O_7 schmilzt inkongruent bei 1590°C und kristalliert in einem monoklinen System mit a = 11.20 Ä, b = 11.94 Ä, c = 7.01 Å, γ = 93.79 und V = 936.97 $Å^3$.