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Phase Equilibria in the System La_2O_3–Na_2O–P_2O_5

II. Binary System La_2O_3–$NaPO_3$

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In the ternary system La_2O_3–Na_2O–P_2O_5 the binary system La_2O_3–$NaPO_3$ has been investigated by thermal, microscopic, X-ray, and dilatometric methods and its phase diagram provided. © 1988 Academic Press, Inc.

The present work is the second part of a study on the ternary system La_2O_3–Na_2O–P_2O_5 and its aim is to determine the phase diagram of the binary system La_2O_3–$NaPO_3$. This system is previously unknown. Only the initial compounds La_2O_3 and $NaPO_3$ have been examined.

Literature reports indicate that lanthanum oxide La_2O_3 occurs in polymorphic modifications of the following structures: hexagonal A-type, hexagonal H-type, monoclinic B-type, regular C-type (*1*, *2*). According to the authors (*3*), only A-type La_2O_3 is stable under atmospheric pressure up to 2040°C. Foex and Traverse (*2*) have reported that the hexagonal A-type is transformed at 2040°C into the hexagonal H-type form. Mehrotra *et al.* (*4*) obtained amorphous La_2O_3 (C-type) by heating $La(OH)_3$ at 400°C under higher pressures.

Sodium metaphosphate $NaPO_3$ melts congruently at 627°C and exhibits polymorphic transitions at 404 and 512°C (*5*).

Experimental

The following initial materials were used for synthesis of sodium–lanthanum phosphates: lanthanum oxide, 99.99% (USRR) and monobasic sodium phosphate $NaH_2PO_4 \cdot H_2O$, analytical grade (POCh). Syntheses were carried out in the solid phase by sintering the initial materials weighed at specific weight ratios. Sodium metaphosphate was prepared from $NaH_2PO_4 \cdot H_2O$ by roasting it for 30 min at 300°C and then at 500°C for 2 hr. Lanthanum oxide La_2O_3 was dried at 800°C. The purity of reagents and phase structure of the substance was controlled microscopically. From melted samples microsections were prepared which were polished and microscopically examined in reflected light.

The binary system La_2O_3–$NaPO_3$ was examined by the thermal, microscopic, X-ray, and dilatometric methods as described in (*6*). A vertical resistance furnace with the tungsten winding on a corundum tube was used for high-temperature thermal studies above 1400°C. The examined samples were prepared as follows: weighed components were mixed in a weighing bottle, ground in an agate mortar, pressed into pellets, placed in platinum (PtRh30, PtIr2) boats, and fused. Temperatures were read by means of an optical pyrometer. The poly-

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morphism and crystal habits of $NaPO_3$ have been investigated and described by several authors.

No analysis for Pt or other crucible materials on the samples brought to equilibrium was carried out. Our experiments did not show any change in the white color of the samples.

Infrared spectra of the preparations from the binary system discussed were measured over the range 400 to 4000 cm^{-1} in a Specord IR-75 spectrophotometer. The samples for studies were prepared in the form of KBr pellets or as Nujol suspensions. The purity of sodium–lanthanum phosphates was checked by chemical analysis (sodium content). Sodium content was determined by the emission flame photometry method in a Perkin–Elmer 403 atomic absorption spectrophotometer using the acetylene–air flame.

Results and Discussion

Studies of the La_2O_3–$NaPO_3$ system were initiated from investigation of the polymorphic transitions in sodium metaphosphate $NaPO_3$. This compound was found to appear in three polymorphic modifications. It was, however, discovered that transitions occur at temperature intervals, viz., α/β at 500–475°C and β/γ at 425–400°C. The phase diagram of the system La_2O_3–$NaPO_3$ developed in our studies is shown in Figs. 1 and 2.

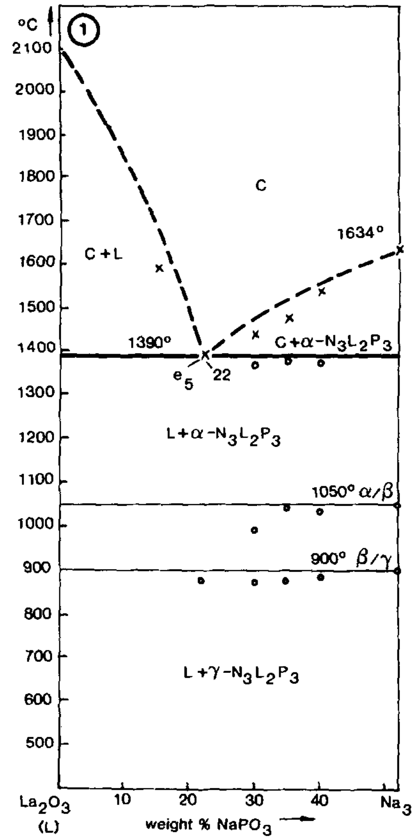
The binary system La_2O_3–$NaPO_3$ was investigated by differential thermal analysis (DTA) during heating and cooling, in the temperature range 20 to 1400°C. The liquidus curve in Fig. 1, shown by a broken line, was derived as follows: the samples were presintered and then heated in platinum (PtRh30) boats in a vertical resistance furnace. The temperature of liquefaction of the samples was determined by means of an optical pyrometer and is shown in Fig. 1 by the symbol x.

The part of the system rich in La_2O_3, containing 80 to 100 wt% of La_2O_3, was examined only in the solid phase because of high melting points. The preparations from this range were synthesized by sintering at 1200°C for 6 hr. The preparations containing 35 to 80 wt% of La_2O_3 were melted in a specially designed furnace with tungsten winding, under argon. The samples rich in $NaPO_3$, over the composition range from 0 to 35 wt% of La_2O_3, were melted in platinum crucibles under air in platinum furnaces. Under the conditions of the experiments performed it was found that La_2O_3 on reacting with $NaPO_3$ yields three unknown compounds at the molar ratio $La_2O_3 : NaPO_3$ equal to 1 : 3, 1 : 4, and 1 : 8. These compounds were assigned the following formulas: $La_2O_3 \cdot 3NaPO_3 = Na_3La_2(PO_4)_3$; $La_2O_3 \cdot 4NaPO_3 = Na_4La_2P_4O_{15}$; $La_2O_3 \cdot 8NaPO_3 = Na_8La_2P_8O_{27}$.

Sodium–lanthanide phosphate $Na_3La_2(PO_4)_3$ was prepared by sintering sodium metaphosphate $NaPO_3$ and lanthanum oxide La_2O_3 in stoichiometric quantities at 900°C for 8 hr. Another method consists in sintering sodium orthophosphate Na_3PO_4 and lanthanum orthophosphate $LaPO_4$ in stoichiometric quantities at 1200°C for 8 hr. $Na_4La_2P_4O_{15}$ is prepared by heating a stoichiometric mixture of La_2O_3 and $NaPO_3$ at 600°C for 8 hr. This phosphate may also be prepared from $Na_4P_2O_7$ and $LaPO_4$ by heating their stoichiometric mixture at 900°C for 24 hr. Sodium–lanthanum phosphate $Na_8La_2P_8O_{27}$ was prepared in the solid phase by sintering sodium phosphate $NaPO_3$ and lanthanum oxide La_2O_3. The components are mixed in stoichiometric quantities and then heated at 600°C for 8 hr.

Purity of the phosphates was checked by the X-ray and IR spectroscopic methods and chemical analysis (sodium content).

We have found that the phosphate $Na_3La_2(PO_4)_3$ melts congruently at 1634°C and appears in the form of three polymorphic modifications with the following transition



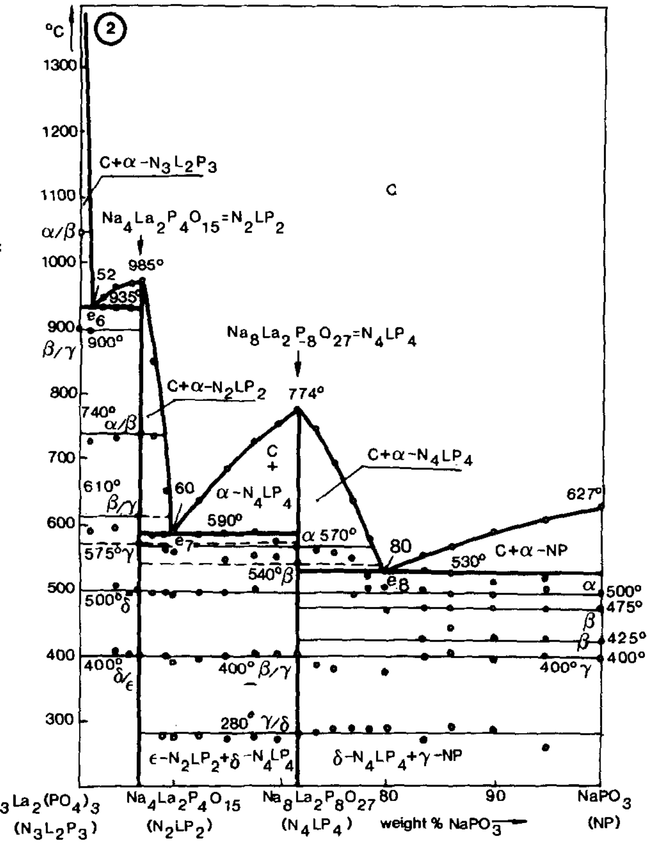


FIG. 1. Phase diagram of the system La_2O_3–$Na_3La_2(PO_4)_3$. ○, Thermal analysis; ×, optical.

FIG. 2. Phase diagram of the system $Na_3La_2(PO_4)_3$–$NaPO_3$. ○, Thermal analysis; ×, optical.

temperatures: α/β at 1050°C and β/γ at 900°C. The transitions were found and examined by thermal analysis of heating and cooling, dilatometric analysis, and high-temperature X-ray. The differential dilatometric curve DTD for $Na_3La_2(PO_4)_3$ within the temperature interval from 20 to 1000°C shows one minimum at 900°C. It also corresponds to one shoulder downward on the TD curve which indicates a transition at 900°C. This transition occurs with a decrease in volume. The total contraction of the sample after cooling down to room temperature is 2.5%. The transition at 1050°C was confirmed by thermal analysis of cooling and heating and is accompanied by a very strong thermal effect. On the grounds of the X-ray powder analysis it was found that the low-temperature modification γ-$Na_3La_2(PO_4)_3$ crystallizes in the rhombic system of the following lattice constants: $a = 5.43$ Å, $b = 12.93$ Å, $c = 18.87$ Å, $v = 1325.13$ Å^3. The high-temperature modification α-$Na_3La_2(PO_4)_3$ crystallizes in the rhombic system of the following lattice constants: $a = 9.14$ Å, $b = 10.83$ Å, $c = 14.69$ Å, $v = 1454.00$ Å^3.

Tables I and II present the lattice constants of the high-temperature modification α-$Na_3La_2(PO_4)_3$ and low-temperature modification γ-$Na_3La_2(PO_4)_3$.

Figure 3 shows the IR spectrum in the range 400 to 1600 cm^{-1} for the following phosphates: $Na_3La_2(PO_4)_3$ measured in

TABLE I

LATTICE CONSTANTS OF THE γ-$Na_3La_2(PO_4)_3$ MODIFICATION (LOW-TEMPERATURE MODIFICATION)

$d_{exp}(\times 10^{-1}$ nm)	$d_{cal}(\times 10^{-1}$ nm)	*hkl*
5.22	5.22	101
4.83	4.83	111
4.69	4.70	102
—	4.72	004
4.42	4.42	112
—	4.43	014
4.19	4.20	031
3.55	3.56	104
—	3.56	033
3.32	3.32	131
3.12	3.12	124
3.01	3.01	115
2.88	2.88	043
2.72	2.72	106
2.61	2.61	202
2.41	2.42	222
—	2.41	107
2.21	2.21	224
—	2.20	205
2.16	2.16	233
—	2.16	060
2.14	2.14	061

Note. Rhombic system: a = 5.43 Å; b = 12.93 Å; c = 18.87 Å; v = 1325.13 Å^3.

TABLE II

LATTICE CONSTANTS OF THE α-$Na_3La_2(PO_4)_3$ MODIFICATION (HIGH-TEMPERATURE MODIFICATION)

$d_{exp}(\times 10^{-1}$ nm)	$d_{cal}(\times 10^{-1}$ nm)	*hkl*
10.81	10.83	010
9.17	9.14	100
8.66	8.72	011
4.66	4.66	120
4.36	4.36	201
—	4.36	022
3.88	3.88	202
3.62	3.61	030
—	3.61	023
3.27	3.27	131
3.23	3.24	032
2.99	2.98	301
2.94	2.93	310
—	2.94	005
2.84	2.84	223
—	2.84	015
2.81	2.81	302
2.60	2.60	140
2.53	2.53	224
2.52	2.51	313
2.30	2.30	331
—	2.30	241
—	2.29	143
2.12	2.12	144
—	2.12	216
2.11	2.10	420
—	2.10	150
2.06	2.06	017
2.03	2.03	413
—	2.03	152
—	2.03	036
1.99	1.99	045
1.97	1.97	334
—	1.97	244
—	1.97	325
1.94	1.94	423
—	1.94	251
—	1.94	404
—	1.94	153
1.85	1.85	236
1.69	1.69	522
—	1.69	336
—	1.69	246
—	1.69	237
1.65	1.65	443
—	1.64	327
1.57	1.57	524

Note. Rhombic system: a = 9.14 Å; b = 10.83 Å; c = 14.69 Å; v = 1454.00 Å^3.

KBr and $Na_4La_2P_4O_{15}$ measured in Nujol. $Na_3La_2(PO_4)_3$ shows clear bands for the valence frequencies of the phosphate group PO_4^{-3} at the following frequency values: 1064, 1020, and 950 cm^{-1}.

Another compound in the binary system discussed is $Na_4La_2P_4O_{15}$. It was found to form congruently at 985°C. The compound absorbs water forming a hydrate of the formula $Na_4La_2P_4O_{15} \cdot 1.5H_2O$. Loss of water occurs at 340°C and the loss in weight is 2.8%. $Na_4La_2P_4O_{15}$ appears in five polymorphic modifications of the following transition temperatures: α/β at 740°, β/γ at 610°C, γ/δ at 575–500°C (the transition occurs at the temperature interval), δ/ε at 400°C. These data were obtained from thermal and dilatometric analyses and confirmed by means of the high-temperature X-ray analysis. The differential dilatometric DTD curves of $Na_4La_2P_4O_{15}$ show three

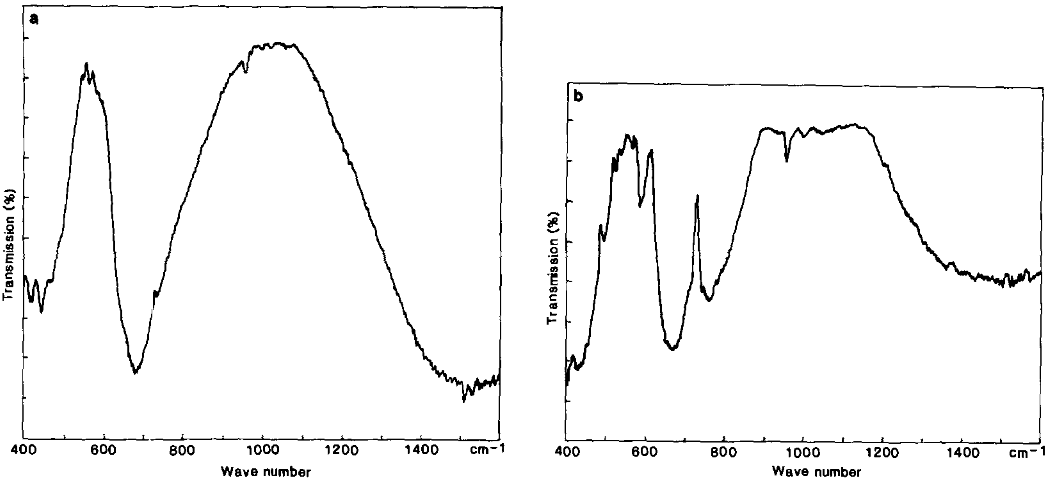


FIG. 3. (a) IRS of $Na_3La_2(PO_4)_3$. (b) IRS of $Na_4La_2P_4O_{15}$.

minima at 400, 600, and 740°C and one maximum at 520°C. The dilatometric TD curve also shows four shoulders: three shoulders downward (for transitions at 400, 600, and 740°C) and one shoulder upward (for a transition at 520°C). The transition at 520°C proceeds with an increase in volume and the resulting elongation of the sample is 1.5%. Other transitions are accompanied by a decrease in volume. The total sample contraction after cooling down to room temperature is 2.5%.

The third compound discovered in our studies is $Na_8La_2P_8O_{27}$. It was found to melt congruently at 774°C and appears in three polymorphic modifications with the following transition temperatures: α/β at 570–540°C, β/γ at 400°C, γ/δ at 280°C. The α/β transition occurs at the temperature interval. The transitions were identified by means of thermal analysis of heating and cooling, dilatometric analysis, and high-temperature X-ray analysis. The differential dilatometric curve shows three minima at 250, 380, and 560°C. The TD curve also shows three shoulders downward which indicates the existence of the above-mentioned transitions. All the transitions found proceed with a decrease in volume and the overall sample contraction after cooling down to room temperature is 10%.

The above-mentioned sodium–lanthanum phosphates divide the La_2O_3–$NaPO_3$ system into four simple partial eutectic systems. In the system La_2O_3–$Na_3La_2(PO_4)_3$ the e_5 eutectic appears at 22 wt% of $NaPO_3$ and at 1590°C.

In another system, $Na_3La_2(PO_4)_3$–$Na_4La_2P_4O_{15}$, the e_6 eutectic consists of 52 wt% of $NaPO_3$ and 48 wt% of La_2O_3 at 935°C. $Na_8La_2P_8O_{27}$ forms eutectic systems with $Na_4La_2P_4O_{15}$ and $NaPO_3$. Eutectic compositions and temperatures are as follows: e_7, 60 wt% of $NaPO_3$ and 40 wt% of La_2O_3 at 590°C and e_8, 80 wt% of $NaPO_3$ and 20 wt% of La_2O_3 at 530°C. The α/β- and β/γ-$NaPO_3$ transitions yield very strong thermal effects over the entire $Na_8La_2P_8O_{27}$–$NaPO_3$ system, the β/γ-$NaPO_3$ transformation yielding a common thermal effect with that of β/γ-$Na_8La_2P_8O_{27}$ at 400°C. The α/β-$Na_8La_2P_8O_{27}$ transition yields a common thermal effect with the e_8 eutectic. The thermal effect from the γ/δ-$Na_8La_2P_8O_{27}$ transition at 280°C is visible over the entire composition range of the $NaPO_3$–$Na_8La_2P_8O_{27}$ and $Na_8La_2P_8O_{27}$–$Na_4La_2P_4O_{15}$ systems as a clear appreciable effect. The transitions of Na_4

$La_2P_4O_{15}$, γ/δ at 575–500°C and δ/ε at 400°C, yield thermal effects only in the range of compositions with the highest concentrations of that phosphate. Thermal effects from the γ/δ-$Na_4La_2P_4O_{15}$ transition coincide with those of the α/β-$Na_8La_2P_8O_{27}$ transition and appear in the form of very large effects over the entire composition range. $Na_3La_2(PO_4)_3$ yields clear effects from the α/β transition at 1050°C and from the β/γ transition at 900°C only in the part rich in $Na_3La_2(PO_4)_3$.

With respect to the difficulties in crystallization the system La_2O_3–$NaPO_3$ may be divided into two parts. In the first part, over the composition range 65–100 wt% of $NaPO_3$, the samples crystallize with difficulties and form glazes if the cooling rate is 5–10°C/min. The samples from that region crystallize fairly well at the cooling rate of 1°C/min. Crystallization is facilitated by frequent grafting with crystals whose composition corresponds to that of the sample examined. In the remaining part of the system, over the composition range from 0 to 65 wt% of $NaPO_3$, the samples crystallize fairly well at the standard cooling rate of 5–10°C/min. The microsections from that system rich in $NaPO_3$ are very hygroscopic. Instead, those with lower $NaPO_3$ concentrations are more resistant to moisture.

References

1. S. R. Roth and S. J. Schneider, *J. Res. Natl. Bur. Stand. Sect. A* **64**(4), 309 (1960).
2. M. Foex and J. R. Traverse, *C.R. Seances Acad. Sci. Ser. C* **262**(8), 636 (1966).
3. J.M. Goldschmidt, F. Ulrich, and T. Barth, *Skr. Nor. Vidensk. Akad. Kl. 1: Mat. Naturvidensk. Kl.*, No. 5 (1926).
4. P. N. Mehrootra, G. V. Chandrashekar, C.N.R. Rao, and E. C. Subbarao, *Trans. Faraday Soc.* **62**(12), 3586 (1966).
5. J. Berak and T. Znamierowska, *Roczniki Chem.* **46,** 1697 (1972).
6. J. Kropiwnicka and T. Znamierowska, submitted for publication.