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PHASE EQUILIBRIA IN THE SYSTEM La_2O_3–Na_2O–P_2O_5: BINARY PHASE DIAGRAM $La(PO_3)_3$–$NaPO_3$

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In the ternary system La_2O_3–Na_2O–P_2O_5, the binary system $La(PO_3)_3$–$NaPO_3$ was examined by means of thermal (heating and cooling), dilatometric, X-ray powder diffraction and microscopic analyses. The occurrence of the phosphate $NaLaP_4O_{12}$ was confirmed and its temperature of congruent melting was determined to be 1174 °C. The powder data indicate a monoclinic system with the lattice constants $a=12.36(6)$; $b=13.45(0)$; $c=6.57(4)$ Å; $\gamma=109.48°$; $V=1030.97$ Å^3. The investigations were carried out on monocrystals.

The binary system $La(PO_3)_3$–$NaPO_3$ in the ternary system La_2O_3–Na_2O–P_2O_5 is known in the literature [1, 2]. Its phase diagram was established via thermal analysis. There is one compound in the system with the formula $NaLa(PO_3)_4$, which forms incongruently at 870°. The eutectic point occurs at 5 mol % LaP_3O_9 at 620° [1]. Palkina reports on $NaLa(PO_3)_4$ as a laser material [3]. According to Tananaew [4], sodium lanthanium polyphosphate also occurs in a hydrated form, as $NaLaP_4O_{12} \cdot 6H_2O$. Its dehydration is a two-stage one and occurs at 140° and 350°. $AgLa(PO_3)_4$, which crystallizes in the monoclinic system $P2_1/c$, $a=12.38$; $b=12.88$; $c=7.33$ Å; $\beta=127.9°$, shows isotypism with $NaLa(PO_3)_4$. $AgLa(PO_3)_4$ occurs in one polymorphic modification [5]. The following group of compounds has also been examined: $NaNd(PO_3)_4 \cdot 7H_2O$; $NaEu(PO_3)_4 \cdot 12H_2O$. These salts form incongruently and undergo multistage dehydration. As a rule, polyphosphates from aqueous solution are obtained by heating metal oxides or their salts with concentrated phosphoric acid [4]. The monocrystal $NaNdP_4O_{12}$ is obtained by the Kyropulos method. Its structure is similar to those of other tetraphosphates, with chains along the sortest directions of the elementary cell. It is a laser material [6]. $NaLa(PO_3)_4$ is said to be isomorphic with $NaNd(PO_3)_4$ [1]. Other polyphosphates, which melt at similar temperatures ($KEuP_4O_{12}$, $KNdP_4O_{12}$, $RbEuP_4O_{12}$, $KLaP_4O_{12}$ and $LiNdP_4O_{12}$), are also known in the literature [6–9, 21]. Data on the fusion temperatures of metaphosphates $Ln(PO_3)_3$ are restricted to [10–12].

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$Ln(PO_3)_3$ occur in two subgroups; according to [14, 15], they crystallize in the orthorhombic system from La to Eu, and in the monoclinic system from Gd to La, including yttrium. The structures of NdP_3O_9 [15], YbP_3O_9 [16] and $La(PO_3)_3$ [17–19] were determined by X-ray structural analysis. NdP_3O_9, belonging in the first subgroup, crystallizes in the space group $C222_1$, $a=11.172$; $b=8.533$; $c=7.284$ Å. The second subgroup $P2_1/c$, $a=11.219$; $b=19.983$; $c=7.284$ Å. The second subgroup includes YbP_3O_9, which crystallizes in the space group $P2_1/c$, $a=11.219$; $b=19.983$; $c=9.999$ Å; $\beta=97.30°$ [16]. $La(PO_3)_3$ is isomorphic with NdP_3O_9 and its full structure has been established [17]. It crystallizes in the space group C222 with the elementary cell parameters $a=11.303$; $b=8.648$; $c=7.397$ Å [18].

According to Balagina [14], the lanthanide metaphosphates $Ln(PO_3)_3$, Ln = Sm, Eu, Ho, Er, Tm, Yb and Lu exhibit various polymorphic forms. For La and Pr, such forms have not been observed.

Experimental

Samples in the system $La(PO_3)_3 - NaPO_3$ were prepared from ready reagents or from reagents synthesized in the laboratory. The following parent substances were used: sodium carbonate Na_2CO_3 (p.a.), lanthanium oxide La_2O_3 (99.9%), ammonium dihydrophosphate $NH_4H_2PO_4$ (p.a.), sodium dihydrophosphate $NaH_2PO_4 \cdot H_2O$.

Anhydrous lanthanum metaphosphate was obtained by sintering a mixture of La_2O_3 and $NH_4H_2PO_4$ at 400° for 5 h [19].

Monocrystals of $La(PO_3)_3$ were prepared by mixing 0.97 g of H_3PO_4 95%, 2.03 g of P_4O_{10} (Merck), 0.04 g of NaF (99.9%, p.a.) and 0.5 g of La_2O_3 (99.9%, USSR); the mixture was heated to 500° at a rate of 5 deg/h, and was then cooled at a rate of 5 deg/h to room temperature. The monocrystals from the mixture were washed with water.

Methods

Simultaneous TG, DTG and DTA determinations on $NaLaP_4O_{12}$ and samples in the binary system were carried out with a derivatograph, with dry air as the atmospheric gas, 10°/min heating rate and Al_2O_3 as reference material.

X-ray analysis at room temperature was carried out by the powder method in the Guinier camera. Infrared absorption spectra was made with using Specord IR 75 (University of Wrocław) spectrophotometer using KBr pellets over the range from 400–4000 cm^{-1}.

Sodium content was determined by the emission flame photometry method in a Perkin–Elmer 403 atomic absorption spectro-photometer using the acetylene—air flame.

Results and discussion

Figure 1 presents a phase diagram of the system $La(PO_3)_3$–$NaPO_3$, which was obtained in our laboratory via thermal (heating and cooling), microscopic and X-ray analyses. Samples for the experiments were prepared from sodium metaphos-

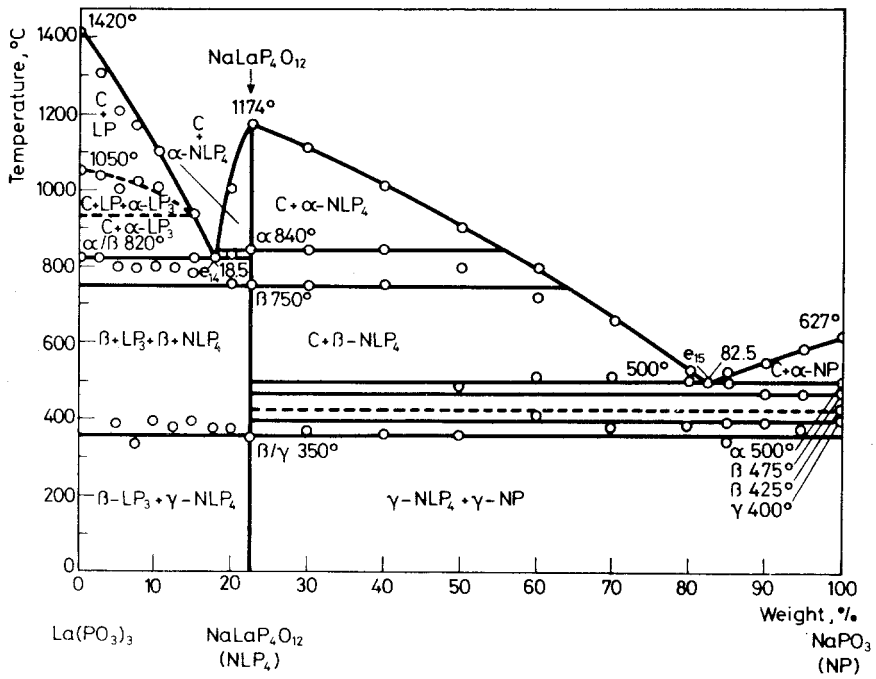

Fig. 1 Phase diagram of the system $La(PO_3)_3$–$NaPO_3$

phate $NaPO_3$ and anhydrous lanthanum metaphosphate $La(PO_3)_3$ according to the methods described in [19]. They were then mixed thoroughly, triturated and sintered at 400° for 6 h. Samples from this system form glazes, decompose quite easily and are hygroscopic. In order to limit the formation of glazes during thermal experiments, grafting and slow cooling were used. However, effects in curves from thermal analysis were not always obtained as a result of such a procedure, which is why samples from the system were also examined visually. Visual observation

Table 1 Lattice parameters of low-temperature γ-$NaLaP_4O_{12}$

$d_{exp} \times 10^{-1}$ nm	$d_{cal} \times 10^{-1}$ nm	*hkl*	$d_{exp} \times 10^{-1}$ nm	$d_{cal} \times 10^{-1}$ nm	*hkl*
6.553	6.574	001	2.501	2.509	302
—	6.563	$1\bar{2}0$	2.456	2.462	222
6.285	6.340	020	—	2.461	411
5.834	5.829	200	—	2.461	240
—	5.836	011	2.424	2.429	132
5.275	5.251	$2\bar{2}0$	2.386	2.396	$3\bar{3}2$
4.959	4.925	110	2.377	2.377	$4\bar{5}0$
4.645	4.645	$1\bar{2}1$	2.299	2.305	241
4.352	4.361	201	2.253	2.244	$4\bar{1}2$
3.936	3.940	121	2.201	2.197	501
—	3.952	$3\bar{2}0$	—	2.202	$4\bar{5}1$
3.889	3.886	300	2.176	2.178	322
3.725	3.717	220	—	2.180	402
3.493	3.491	$3\bar{1}1$	2.145	2.145	$1\bar{1}3$
—	3.503	$2\bar{3}1$	—	2.144	142
—	3.501	330	—	2.150	$5\bar{4}1$
3.298	3.287	002	2.131	2.132	340
—	3.281	$2\bar{4}0$	2.107	2.113	060
3.222	3.236	221	2.072	2.071	023
3.064	3.073	$4\bar{1}0$	—	2.072	$1\bar{5}2$
—	3.064	$4\bar{2}0$	—	2.074	$2\bar{5}2$
3.028	3.027	311	—	2.076	$3\bar{6}1$
3.007	3.006	112	—	2.070	$4\bar{6}0$
2.979	2.981	230	2.058	2.059	511
—	2.988	$1\bar{4}1$	—	2.060	$6\bar{2}0$
2.932	2.939	$1\bar{2}2$	2.045	2.042	$6\bar{3}0$
—	2.936	$2\bar{4}1$	1.982	1.979	332
2.913	2.918	022	—	1.984	520
—	2.090	320	1.986	1.986	$1\bar{3}3$
—	2.914	400	—	1.970	242
2.836	2.829	140	—	1.967	160
2.787	2.786	$2\bar{2}2$	—	1.966	$6\bar{2}1$
—	2.784	$4\bar{1}1$	1.956	1.960	$5\bar{1}2$
2.739	2.733	122	1.945	1.945	033
2.677	2.674	$2\bar{5}0$	—	1.943	600
2.677	2.669	$1\bar{5}0$	—	1.943	$5\bar{3}2$
2.654	2.660	321	1.936	1.934	$3\bar{1}3$
—	2.653	410	—	1.936	$2\bar{3}3$
2.654	2.650	$1\bar{3}2$	—	1.934	$6\bar{1}1$
—	2.647	$4\bar{3}1$	1.876	1.873	$6\bar{5}0$
2.556	2.548	$3\bar{5}0$	1.863	1.863	601
2.529	2.527	$3\bar{2}2$	1.855	1.857	$3\bar{3}3$
—	2.536	050	1.841	1.843	313

$d_{exp} \times 10^{-1}$ nm	$d_{cal} \times 10^{-1}$ nm	*hkl*	$d_{exp} \times 10^{-1}$ nm	$d_{cal} \times 10^{-1}$ nm	*hkl*
—	1.839	271	—	1.739	261
—	1.839	561	—	1.738	570
1.811	1.810	512	1.712	1.705	170
—	1.811	070	1.701	1.698	522
—	1.814	171	—	1.701	721
1.803	1.802	043	—	1.702	731
—	1.803	530	1.645	1.643	004
—	1.803	260	—	1.646	372
—	1.801	651	—	1.645	180
1.793	1.789	342	1.579	1.581	204
1.878	1.788	441	1.579	1.581	204
—	1.788	351	—	1.580	532
1.771	1.768	$3\bar{4}3$	—	1.581	262
—	1.770	$5\bar{5}2$	—	1.578	543
—	1.769	$4\bar{7}1$	—	1.578	580
1.754	1.751	$4\bar{6}2$	1.523	1.521	063
1.740	1.738	531			

Monoclinic system: $a = 12.36(6)$ Å, $b = 13.45(0)$ Å, $c = 6.57(4)$ Å, $\gamma = 109{,}48°$, $V = 1030.97$ Å^3

involved recording of the temperature at which the first traces of liquid were noticed, and the temperature at which the sample liquefies totally and becomes transparent. On the basis of the experiments, we confirmed that $La(PO_3)_3$ and $NaPO_3$ form a known compound in the molar ratio 1 : 1, with formula $NaLaP_4O_{12}$, which melts congruently at 1174° [19]. The experiments were carried out with monocrystals of $NaLaP_4O_{12}$. This compound can be obtained by two methods: 1) from anhydrous sodium metaphosphate $NaPO_3$ and lanthanum metaphosphate $La(PO_3)_3$ by the sintering of these compounds in stoichiometric amounts at 600° for 10 h; 2) from the ready substances mentioned in the experimental, crystalline $NaLaP_4O_{12}$ was obtained [20]. The purity of the compound was checked by means of X-ray and IR spectroscopy. Figure 2 depicts monocrystals of $NaLaP_4O_{12}$ obtained by the methods described in [20].

Figure 3 shows a microphotograph of a sample of $NaLaP_4O_{12}$. Originally educed, large, white crystals of $NaLaP_4O_{12}$, with sharp edges can be seen against the background of glass (grey area).

Investigations of $NaLaP_4O_{12}$ in the solid phase showed that it occurs in three polymorphic transformations, with the following transformation temperatures: 840°, 750° and 350°. A high-temperature transformation occurs above 840°. The transitions were examined by means of thermal (heating and cooling) and dilatometric analyses. The differential curve DTA shows three minima, at 840°, 750° and 350°. The TG curve also shows three bends downwards, which confirms

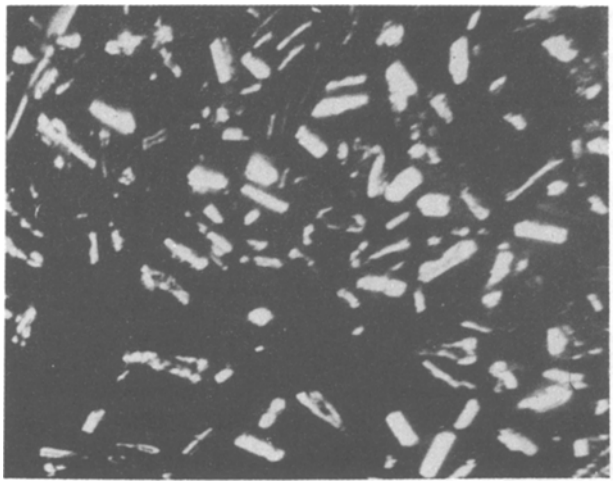

Fig. 2 The monocrystals of $NaLaP_4O_{12}$ (polarized light, magnification 140×, size 0.05 mm)

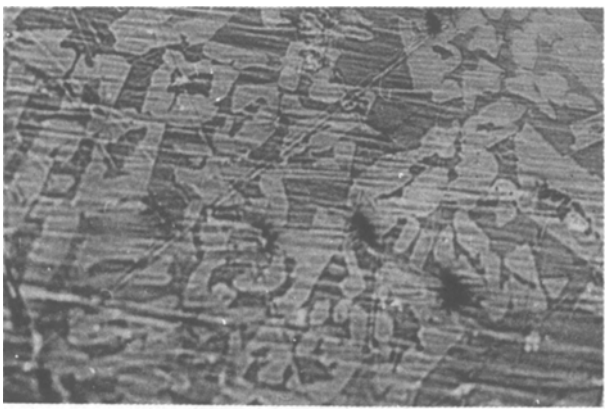

Fig. 3 Microphotography of the sample of a compound composition $NaLaP_4O_{12}$

that the above transformations proceed with volume decrease. The total contraction of the sample is 3%. With $La(PO_3)_3$, $NaLaP_4O_{12}$ the eutectic composition e14: 18.5 wt.% $NaPO_3$ and 81.5 wt.% $La(PO_3)_3$ at 820°. A peritectic reaction proceeds in this system in the composition range from 0 to 15 wt.% $NaPO_3$. The $NaLaP_4O_{12}$–$NaPO_3$ system has a eutectic character as well. Eutectic e15 occurs at 82.5 wt.% $NaPO_3$ and 17.5 wt.% $La(PO_3)_3$ at 500°.

The $La(PO_3)_3$ $NaLaP_4O_{12}$ system does not have all the characteristics of a

binary system, because of the peritectic formation of lanthanum metaphosphate. Liquid C, together with lanthanum orthophosphate, yields crystals of $La(PO_3)_3$.

The transformation α- to β-$NaLaP_4O_{12}$ (840–750°) is manifested as a strong thermal effect in the heating curves in the entire composition range. In the $La(PO_3)_3 - NaLaP_4O_{12}$ system, it gives a common effect with the eutectic. The β- to γ-$NaLaP_4O_{12}$ transformation at 350° gives a common effect with the β- to γ-$NaPO_3$ transformation in the entire composition range.

The effect of the α- to β-$NaPO_3$ transformation at 475–500° covers the thermal effect from eutectic e15 effect. The thermal effect of the α- to β-$La(PO_3)_3$ transformation at 820° covers the eutectic e14 effect. According to Ben Hassen et al. [1], $NaLa(PO_3)_4$ is formed incongruently at 870°. In an analysis of the $La(PO_3)_3$ system, these authors used the hydrated lanthanum metaphosphate $LaP_3O_9 \cdot 3H_2O$ obtained from aqueous solution by the Serra [22] method. Lanthanum polyphosphates (mainly LaP_5O_{14}) as a result of heating to 500° [20]. It can be concluded that the authors of [1] carried out experiments with a complex multiphase system, which resulted in the disagreement between their results and those obtained in our laboratory [19]. According to Fedorowa [2], $NaLa(PO_3)_4$ gives a eutectic with $NaPO_3$ at 580°. X-ray powder data on $NaLaP_4O_{12}$ indicate an orthorhombic system with the following lattice constants: $a = 10.10$; $b = 13.20$; $c = 7.216$ Å. The experiments on the monocrystals of $NaLaP_4O_{12}$ carried out in our laboratory show that the powder X-ray data differ markedly from those in the literature [1, 2]. Table 1 gives the lattice parameters of the low-temperature variety of γ-$NaLaP_4O_{12}$. The powder data point to a monoclinic system with the lattice constants: $a = 12.36(6)$, $b = 13.45(0)$, $c = 6.57(4)$ Å; $\gamma = 109.48°$; $V = 1030.97$ Å^3.

Powder data were obtained through use of the "Powder" program, version IBM 360/05 (1974) [23].

During our experiments we discovered that lanthanum metaphosphate undergoes a so far unknown transformation at 820°. This proceeds with great difficulty in pure $La(PO_3)_3$. The addition of sodium lanthanum phosphates $Na_4La_2P_4O_{15}$, $Na_8La_2P_8O_{27}$ or $NaLaP_4O_{12}$ in amounts of from 2.0 to 2.5 wt.% accelerates the transformation and increases the thermal effect which accompanies it [18].

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Zusammenfassung — Das binäre Teilsystem $La(PO_3)_3$–$NaPO_3$ des ternären Systemes La_2O_3–Na_2O–P_2O_5 wurde mittels thermischer, dilatometrischer, Röntgendiffraktions- und mikroskopischen Methoden untersucht. Es wurde die Existenz des Phosphates $NaLaP_4O_{12}$ und dessen kongruenter Schmelzpunkt von 1174 °C festgestellt. Die Röntgendiffraktionsaufnahmen lassen auf ein monoklines System mit den Gitterkonstanten $a = 12{,}36(6)$, $b = 13{,}45(0)$, $c = 6{,}57(4)$ Å, $\gamma = 109{,}48°$ und $V = 1030{,}87$ Å^3 schliessen. Die Untersuchungen wurden an Einkristallen durchgeführt.

Резюме — С помощью термического (нагревание и охлаждение), дилатометрического, рентгенофазового и микроскопического анализов исследована бинарная система $La(PO_3)_3$–$NaPO_3$, образующаяся в тройной системе La_2O_3–Na_2O–P_2O_5. Подтверждено образование безводного полифосфата $NaLaP_4O_{12}$, плавящегося конгруэнтно при 1174°. Данное соединение находится в трех полиморфных модификациях γ-, β- и α-при температурах, соотвстственно, 350, 750 и 840°. Полифосфат $NaLaP_4O_{12}$ кристаллизуется в моноклинной сингонии с параметрами решетки $a = 12{,}36$ Å, $b = 13{,}45$ Å, $c = 6{,}57$ Å, $\gamma = 109{,}48°$ и $V = 1030{,}97$ Å^3. Бинарная система образует две эвтектики при температурах 500 и 820. Метафосфат лантана $La(PO_3)_3$ плавится инконгруэнтно при 1050°, а при 820° — претерпевает α-, β-полуморфное превращение. Добавление 2–2,5 весовых % лантанонатриевых фосфатов увеличивает термический эффект такого полиморфного превращения.