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PHASE EQUILIBRIUM IN THE SYSTEM $Na_5P_3O_{10}$-$Na_8La_2(PO_3)_8O_3$

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The phase diagram $Na_8La_2(PO_3)_8O_3$-$Na_5P_3O_{10}$, which comprises part of the ternary system La_2O_3-Na_2O-P_2O_5, was constructed in the laboratory. The oxyphosphate $Na_8La_2(PO_3)_8O_3$ crystallizes in the orthorombic system; the lattice parameters are as follows a = 8.96(4)Å, b = 9.35(8)Å, c = 12.29(7)Å.

A great number of rare-earth compounds exhibit fluorescence, in different light ranges, and display very good laser properties [1-3]. Fluorescence effects are observed in a stoichiometric compound with a high concentration of active Eu^{3+} and Nd^{3+} in the rare-earth pentaphosphates.

Investigations on the binary system Na_2O-P_2O_5 were first made many years ago, and primarily revealed polyphosphates. Papers [4-6] report that only one sodium polyphosphate occurs, with the formula Na_5P_3O. The binary system $Na_4P_2O_7$-$NaPO_3$ has been examined by numerous authors [7-10]. Berak *et al.* confirmed the existence of $Na_5P_3O_{10}$ in this range, which melts incogruently at 620° and occurs in two polymorphic modifications at 529°. The oxyphosphate $Na_8La_2(PO_3)_8O_3$ was synthesized for the first time by Kropiwnicka [12].

The product is characterized by polimorphic α, β, γ and δ phases with the following transition temperatures: 570-540°, 400°, 280° and congruent

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melting at 774° [11]. The solid phases in the equilibrium system Na_2O-P_2O_5-H_2O near 300° have been reported by Taylor *et al.* [12].

Experimental

The starting materials were: sodium metaphosphate $NaPO_3$, oxide La_2O_3 99.9% (USSR) and sodium pyrophosphate $Na_4P_2O_7$. The oxyphosphate $Na_8La_2(PO_3)_8O_3$ was obtained by synthesis in a solid-state reaction. The stoichiometric mixture of La_2O_3 and $NaPO_3$ was ground in an agate mortar, pressed into pellets and heated in air in the interval 400-600° for 8 hours.

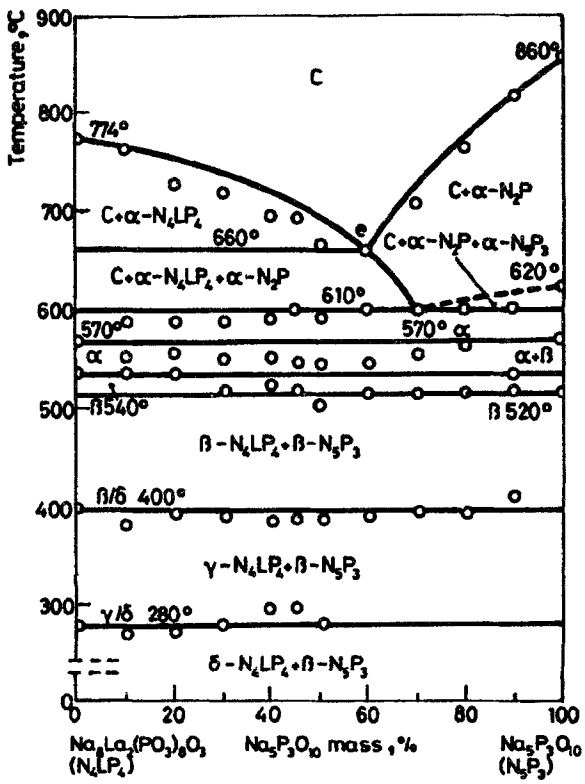

Fig.1 Phase diagram of the system $Na_8La_2(PO_3)_8O_3$-$Na_5P_3O_{10}$ o - thermal analysis

Table 1 Powder diffraction data on the low-temperature $Na_8La_2(PO_3)_8O_3$ phase

d exp. (x 10^{-1} nm)	d calc.(x 10^{-1} nm)	hkl
4.461	4.482	200
-	4.458	112
3.723	3.723	022
-	3.727	103
3.463	3.438	122
-	3.463	113
3.232	3.236	220
3.122	3.119	030
-	3.130	221
3.016	3.023	031
-	3.024	203
2,692	2.687	302
2.535	2.540	223
-	2.535	204
2.263	2.263	140
2.203	2.204	401
2.035	2.036	332
-	2.032	043
1.954	1.958	225
-	1.953	116
1.929	1.931	035
1.851	1.850	051
-	1.850	243
1.810	1.812	151
-	1.812	423
-	1.810	404
1.790	1.792	500
-	1.790	052
1.778	1.778	414
1.745	1.743	511
-	1.745	432
1.721	1.721	502
-	1.719	244
-	1.723	107
1.692	1.692	512
-	1.695	045
-	1.690	306
-	1.695	117

Table 1 cont.

d exp. ($x10^{-1}$ nm)	d calc.($x10^{-1}$ nm)	hkl
1.664	1.662	252
-	1.663	433
-	1.665	145
-	1.663	316
1.645	1.642	503
-	1.644	027
1.605	1.604	441
1.574	1.573	351
-	1.573	154
1.512	1.511	062
-	1.512	406
-	1.514	307
1.505	1.507	532
-	1.505	443
-	1.505	254

orthorhombic system; a = 8.96(4)Å, b = 9.35(8)Å, c = 12.29(7)Å

The powder of La_2O_3 was calcined at 900° typically for 2 days before weighing. The polyphosphate $Na_5P_3O_{10}$ was synthesized from $NaPO_3$ and $Na_4P_2O_7$ in 1:1 stoichiometric molar ratio in two stages:

1. at 250° for 2 hours;
2. at 400° for 5 hours.

The oxyphosphate $Na_8La_2(PO_3)_8O_3$ [12] was also used as a starting material. Samples in the binary system were synthesized by the reaction between $Na_8La_2(PO_3)_8O_3$ and $Na_5P_3O_{10}$ at 500° for 6 hours in an open platinum and gold crucible.

Temperature was measured with a $Pt/PtRh_{10}$ thermocouple, calibrated against the solidification point of K_2SO_4 (1076°). In thermal studies involving heating, MOM 3427 derivatograph was used with photographic recording over the temperature range from 20 to 1000°. The operating conditions used were as follos: sensitivity TG 500 mg, DTA-1/5, DTG-1/10, heating rate 10 deg/min. Al_2O_3 was used as a reference material. In the thermal studies involving cooling, an LP 839 temperature programmer (Chinoin Budapest) was used. The rate of cooling was 10 deg/h. Infrared absorption data were obtained with a Specord IR 75 instrument (University of Wroclaw). The

samples were pressed in KBr pellets. No pyrophosphate or ortophosphate impurity could be detected.

Unit cell parameters for $Na_5P_3O_{10}$ and $Na_8La_2(PO_3)_8O_3$ were determined from Guinier photographs, taken with CuKα radiation (mean λ = 1.5418Å). Intensities were estimated visually.

Results and discussion

The purpose of this work is to report an unknown pseudobinary system $Na_8La_2(PO_3)_8O_3$-$Na_5P_3O_{10}$ and to present X-ray powder diffraction data on sodium-lanthanum phosphates. The phase diagram of the system $Na_8La_2(PO_3)_8O_3$-$Na_5P_3O_{10}$ is shown in Fig. 1.

$Na_5P_3O_{10}$ forms incongruently in the system $Na_4P_2O_7$-$NaPO_3$ and melts incongruently in this system at 620° (see also [10]). In the pseudobinary system, we deal with the ternary peritectic reaction:

$$C + \alpha\text{-}Na_4P_2O_7 = \alpha\text{-}Na_5P_3O_{10} + \alpha\text{-}Na_8La_2(PO_3)_8O_3$$

in which liquid C reacts with crystalline $Na_4P_2O_7$. Crystalline $Na_5P_3O_{10}$ and $Na_8La_2(PO_3)_8O_3$ are formed. The reaction proceeds in accordance with the phase rule. Below 610°, only two phases exist: α-$Na_8La_2(PO_3)_8O_3$ and α-$Na_5P_3O_{10}$, crystallizing as glasses. The system was examined by thermal analysis, involving heating and cooling of the previously melted samples. The phase transitions $Na_8La_2(PO_3)_8O_3$ were reported in [10, 12].

$Na_5P_3O_{10}$ occurs in two polymorphic modifications: α-$Na_5P_3O_{10}$ above 570° and β-$Na_5P_3O_{10}$ below 520°. The high-temperature phase α-$Na_5P_3O_{10}$ is stabilized by $Na_8La_2(PO_3)_8O_3$; it is thermodynamically unstable at lower temperatures. In this case we are dealing with a substitution transition which could be connected with an order-disorder transition. The phase-transitions α/β-$Na_8La_2(PO_3)_8O_3$ (570-540°) and α/β-$Na_5P_3O_{10}$ give endothermic effects throughout the examined range. The phase transition β/γ-$Na_8La_2(PO_3)_8O_3$ at 400° produces a single, very strong exothermic effect for the whole range of compositions examined.

The thermal effects from the phase-transition γ/δ -$Na_8La_2(PO_3)_8O_3$ at 280° are contained in the $Na_8La_2(PO_3)_8O_3$ richer part of the system. The samples in this system are hygroscopic, which makes their microscopic study difficult.

$Na_8La_2(PO_3)_8O_3$ exhibits typical wide multiplet bands in the range 400-560 cm^{-1}, which are also observed in the spectrum of La_2O_3, and frequencies of the inherent vibrations of phosphate groups: 1099 cm^{-1} (vs.) and 1150 cm^{-1} (vs.). $Na_8La_2(PO_3)_8O_3$ crystallizes in the orthorhombic system, with the unit-cell parameters a = 8.96(4)Å, b = 9.35(8)Å, c = 12.29(7)Å. Table 1 gives the powder diffraction data for $Na_8La_2(PO_3)_8O_3$.

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Zusammenfassung - Es wurde das Phasendiagramm $Na_8La_2(PO_3)_8O_3$ - $Na_5P_3O_{10}$, welches einen Teil des ternären Systemes La_2O_3 - Na_2O - P_2O_5 enthält, konstruiert. Das Oxyphosphat $Na_8La_2(PO_3)_8O_3$ kristallisiert rhombisch mit folgenden Gitterkonstanten: a = 8.96(4)Å, b = 9.35(8)Å, c = 12.29(7)Å.