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# Study of Phase Equilibria in the System $Nd_2O_3$–$Na_2O$–$P_2O_5$. The Partial System $NdPO_4$–$NaPO_3$–$Nd(PO_3)_3$

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A partial system of $NdPO_4$–$NaPO_3$–$Nd(PO_3)_3$ in the ternary system $Nd_2O_3$–$Na_2O$–$P_2O_5$ was investigated and its phase diagram is proposed. Thermoanalytical methods and X-ray powder diffraction were employed. In the composition range under examination, two ternary compounds occur, which melt incongruently and have the formulae $NaNd(PO_3)_4$ (m.p. 866°C) and $NaNdP_2O_7$ (m.p. 790°C). Two quasi-binary sections, $NdPO_4$–$NaNd(PO_3)_4$ and $NaNdP_2O_7$–$NaNd(PO_3)_4$ have been identified.

**Key words:** phase equilibria, neodymium-sodium phosphates

The ternary system $Nd_2O_3$–$Na_2O$–$P_2O_5$ is being the object of our long-term work in study of the phase equlibria involved. The present paper discusses the results concerning the area bounded by the compounds $NdPO_4$, $Nd(PO_3)_3$, $NaPO_3$. The composition range is surrounded by three side systems: (1) $NdPO_4$–$Nd(PO_3)_3$, (2) $Nd(PO_3)_3$–$NaPO_3$, (3) $NdPO_4$–$NaPO_3$. Phase diagrams of the first two systems were known [1,2,3]. The $NdPO_4$ and $Nd(PO_3)_3$ phosphates constitute a simple eutectic system [1]. Its eutectic point parameters are: composition 97.5 wt. % $Nd(PO_3)_3$, 2.5 wt. % $NdPO_4$; melting point 1253°C [2]. According to [3], an intermediate compound of $NaNd(PO_3)_4$ occurs in the system $Nd(PO_3)_3$–$NaPO_3$. It melts incongruently at 866°C and with $NaPO_3$ metaphosphate gives the eutectic of the composition 85 wt. % $NaPO_3$, 15 wt. % $Nd(PO_3)_3$, which melts at 618°C. Phase diagram of the third side system was not known.

Literature indicates that a binary phosphate, with the formula $NaNdP_2O_7$, exists. In view of its stoichiometry it may occur in the system $NdPO_4$–$NaPO_3$. The structure and the compound were described in [4], showing that $NaNdP_2O_7$ decomposes at 790°C, according to the reaction $NaNdP_2O_7$ (solid) → $NdPO_4$ (solid) + $NaPO_3$ (amorphous). It crystallizes in the monoclinic system with lattice parameters $a = 12.613(1)$, $b = 8.538(8)$, $c = 5.267(4)$ Å, $\beta = 90.79(4)°$.

## EXPERIMENTAL

The ternary partial system $NdPO_4$–$Nd(PO_3)_3$–$NaPO_3$ was investigated by thermoanalytical methods (DTA, TG, DTG) and X-ray powder diffraction. Used were off-the-shelf commercial reagents of analytical purity: $Nd_2O_3$ (99.99%), $H_3PO_4$ (85%), $NaH_2PO_4 \cdot H_2O$, $(NH_4)_2HPO_4$. From those reagents, the phosphates $NaPO_3$, $Nd(PO_3)_3$, $NaNd(PO_3)_4$, $NdPO_4$ were synthesized.

Sodium metaphosphate $NaPO_3$ was obtained *via* full dehydratation of $NaH_2PO_4 \cdot H_2O$ at 300°C for 1 h and at 500°C for 1 h. Neodymium metaphosphate $Nd(PO_3)_3$ was synthesized *via* solid-state reaction from $Nd_2O_3$ and $(NH_4)_2HPO_4$ mixed in the molar ratio 1:6 [3]. $NaNd(PO_3)_4$ phosphate was produced by heating an equimolar mixture of $Nd(PO_3)_3$ and $NaPO_3$ kept in the temperature range 600–650°C for 12 h [3].

Samples for thermoanalytical investigation were presynthesized *via* the solid-state recation. The substrates, weighed in predetermined amounts, were thoroughly mixed, rubbed in an agate mortar, and sintered. The conditions of presynthesis (*i.e.* temperature and the sintering period) were found experimentally. The thermoanalytical investigations were performed by using a SETSYS$^{TM}$ calorimeter (TG-DSC; SETARAM) up to 1500°C (scanning rate 10 $Kmin^{-1}$), in an argon atmosphere and platinum crucibles; sample weight 0.001–0.018 g. Sporadically also, a derivatograph type 3427 (MOM, Hungary) was used up to 1350°C (scanning rate 5 $K \cdot min^{-1}$) in air, platinium crucibles with $Al_2O_3$ p.a. as the standard substance; weight of samples was 0.4–0.6 g. Phase purity of the parent substances used and the phase composition of the samples presynthesized (sinters) was controlled by X-ray powder analysis. The X-ray diffraction method was also employed to identify the phases that were formed in the partial system of interest. SIEMENS D 5000 and B-TUR M62 diffractometer were used ($CuK_\alpha$ radiation).

## RESULTS AND DISCUSSION

Among the three side systems, that surround the partial system $NdPO_4$–$Nd(PO_3)_3$–$NaPO_3$, only one phase diagram of $NdPO_4$–$NaPO_3$ system was unknown. In the first stage of the experimental work, an attempt was made to establish phase equilibria for this side system. The necessary initial step was to answer the question, whether the intermediate compound of the formula $NaNdP_2O_7$ (known in the literature) occurs in the system of interest. The empirical formula of the phosphate implies the molar ratio $NdPO_4$:$NaPO_3$ equal to 1:1 (29.9 wt. % $NaPO_3$, 70.1 wt. % $NdPO_4$). Accordingly, we made an attempt to obtain the compound by the conventional method of solid-state reaction, by using $NdPO_4$ and $NaPO_3$ as parent substance. In that attempt, an equimolar mixture of the compounds was heated at different temperatures for different periods. Phase composition of sinters obtained was identified each time by X-ray powder diffraction. It was found that this method did not yield the expected result of the $NaNdP_2O_7$ phosphate of phase purity. Employing the method of [4], we finally obtained the positive result (*i.e.* $NaNdP_2O_7$ phase purity). In accordance with the results of those authors, $NaNdP_2O_7$ phosphate melts incongruently at 790°C, giving crystals of $NdPO_4$ and an $NaPO_3$-rich liquid. In view of the difficulties in obtaining $NaNdP_2O_7$ phosphate from $NdPO_4$ and $NaPO_3$ *via* solid-state reaction, we had to use two series of samples to determine the phase equilibria and to construct the phase diagram of the $NdPO_4$–$NaPO_3$: (i) heteromolar mixtures of $NdPO_4$ and $NaNdP_2O_7$ (in order to determine phase equilibria in the composition range 0–29 wt. % $NaPO_3$); (ii) heteromolar mixtures of $NaNdP_2O_7$ and $NaPO_3$ (to determine phase equilibria in the composition range 30–100 wt. % $NaPO_3$). The above mixtures were presynthesized *via* solid-state reaction. The experimental conditions employed were differentiated: The $NdPO_4$-rich samples (series (i)), were heated at 700°C for 96 h; the $NaPO_3$-rich ones were heated at 550°C for 12 h. The sinters obtained were crushed and thoroughly rubbed. Their phase composition was each time controlled X-ray

diffraction. Then the sinters were subjected to thermoanalytical investigations. It was found, that DTA curves showed one endothermic effect or two, dependent on sample's composition. The DTA curves, nearly in the entire composition range (*i.e.* up to 90 wt. % $NaPO_3$), revealed a peak corresponding to a temperature of about 790°C. The peak has been ascribed to a peritectic reaction, which proceeds according to the network $NaNdP_2O_7 \rightarrow NdPO_4$ + liquid. A strong, extra endothermic effect was present on the DTA curves for the samples of the composition in the area between the $NaNdP_2O_7$ and $NaPO_3$ compounds. The corresponding temperature was about 620°C. The effect has been attributed to an eutectic phase transition. It should be noted, that any thermal effects connected with melting have not been detected for the samples on any DTA curve. This negative result makes the finding of the true shape of the liquidus curve impossible. Based on the above results, a phase diagram of the system $NdPO_4$–$NaPO_3$ is presented in Fig. 1. The liquidus curve has a suggested form and is drawn by dashed line. Parameters of the eutectic point are: 95 wt. % $NaPO_3$, 5 wt. % $NdPO_4$; melting point 623°C. The peritectic reaction ends at about 90 wt. % $NaPO_3$. Pure sodium metaphosphate $NaPO_3$ appears in three polymorphic modifications with transition points of 510°C for the $\alpha/\beta$ and 404°C for the $\beta/\gamma$. No accompanying thermic effect was, however, present on the DTA-heating curves for the samples of the system under discussion.

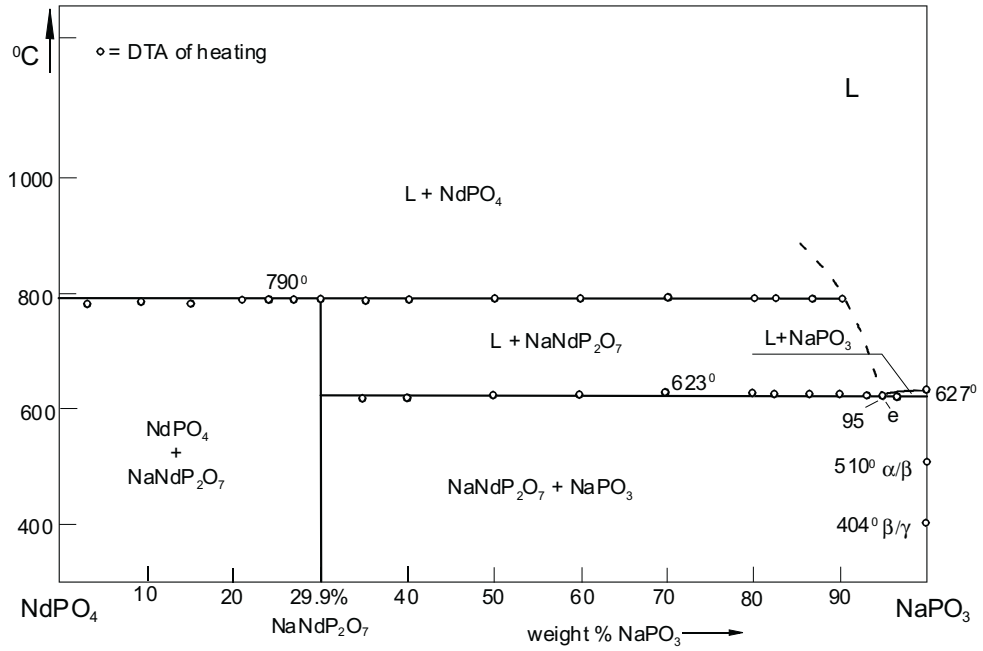


**Figure 1.** Phase relations in the system $NdPO_4$–$NaPO_3$.

An accurate determination of phase equilibria, in the partial system $NdPO_4$–$NaPO_3$–$Nd(PO_3)_3$ in the whole range of composition and temperature, was difficult. Problems, that arised during the course of experimental work, are discussed in the following. The samples were prepared from different compounds: $NdPO_4$, $Nd(PO_3)_3$, $NaPO_3$, $NaNd(PO_3)_4$, $NaNdP_2O_7$. For presynthesis, heteromolar mixtures of the above phosphates were heated at different temperatures (in the solid phase) for different periods. Phase composition of the sinters was identified by X-ray. In this way it has been found, that two quasi-binary sections, $NdPO_4$–$NaNd(PO_3)_4$ and $NaNdP_2O_7$–$NaNd(PO_3)_4$, occur in the partial system under discussion.

The experimental work started, with examining phase equilibria of the section $NdPO_4$–$NaNd(PO_3)_4$. The samples were prepared from the parent phosphates. Heteromolar mixtures of the compounds were presynthesized by heating at 750°C for 12 h, which was followed by the routine X-ray control of sinters produced. The sinters were examined by DTA-heating. A strong endothermic effect was observed on DTA curves in the composition range under investigation, with a temperature of about 866°C, corresponding to it. Moreover, for samples containing 60–75 wt. % $NaNd(PO_3)_4$, it was noted, that the effect split into two directly consecutive endothermic effects. The temperature corresponding to this extra effect was 850–860°C. $NaNd(PO_3)_4$-rich samples, in turn, revealed rather a diffuse effect, which could be ascribed to the melting process of the samples. The results, however, were insufficient to construct a phase diagram of the $NdPO_4$–$NaNd(PO_3)_4$ section. Next, an attempt was made to identify the phases, present in temperatures above 866 °C. X-ray analysis of frozen samples showed the presence of $NdPO_4$ and $Nd(PO_3)_3$ phosphates in those samples. Hence, we conclude, that the section $NdPO_4$–$NaNd(PO_3)_4$ is the real quasi-binary system only in the subsolidus area. At a higher temperature, it has a multiphase character. Consequently, Fig. 2 represents only data obtained from DTA-heating of precalcined samples of the section in question. A plausible, theoretical phase diagram of the $NdPO_4$–$NaNd(PO_3)_4$ system is shown by the inset in the upper-left corner of the figure.

Determining the phase equilibria for the other section, $NaNdP_2O_7$–$NaNd(PO_3)_4$, was complicated like the former case. Samples for this investigation were prepared from parent phosphates. Heteromolar mixtures of the compounds were presynthesized by heating at 650–700°C for 12 h. The sinters obtained were examined by DTA-heating. This resulted in the following: A strong endothermic effect was revealed on the DTA curves in the entire composition range of the section under discussion with the corresponding temperature, varying between 758 and 767°C, dependent on the composition. For samples of composition in the range from about 50 to 100 wt. % $NaNd(PO_3)_4$, the DTA-heating curves additionally showed two strong consecutive endothermic effects with a corresponding temperature of 840–865°C. In contrast, a sample of the composition 30 wt. % $NaNd(PO_3)_4$ produced a DTA curve, showing two distinct consecutive effects with their corresponding temperatures of 760 and 780°C. It should be noted, that any thermal effects above 865°C have not be detected on any DTA curve.

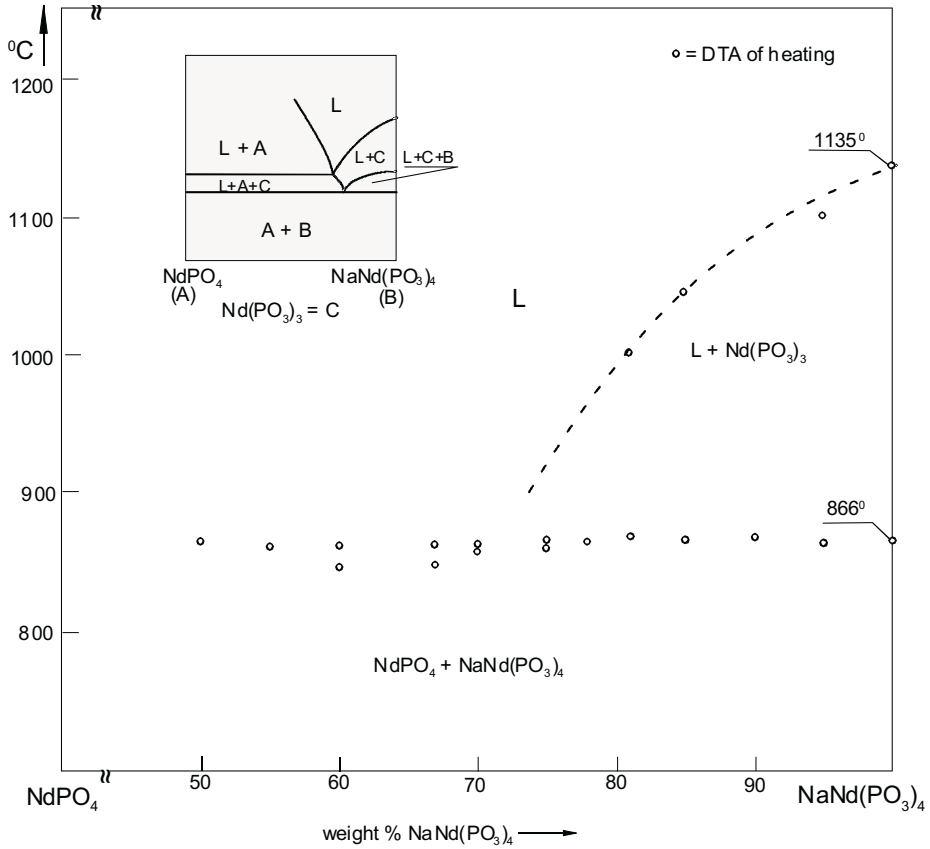


**Figure 2.** DTA-heating data for precalcined samples with the quasi-binary section $NdPO_4$–$NaNd(PO_3)_4$.

The thermoanalytical examination and X-ray phase analysis were essential to interpret the results under discussion, in which the following presynthesized samples were used: (i) heteromolar mixtures of phosphates, $NaNd(PO_3)_4$, $NaNdP_2O_7$, $NaPO_3$; (ii) heteromolar mixtures of phosphates $NdPO_4$, $Nd(PO_3)_3$, $NaNdP_2O_7$, $NaNd(PO_3)_4$. An analysis of these complex results leads to a suggested phase diagram of the $NaNdP_2O_7$–$NaNd(PO_3)_4$ section, which is shown in Fig. 3. The section is a real quasi-binary system only in the subsolidus area, *i.e.* below a temperature of about 765°C. In the high-temperature area, it shows a multiphase character. The suggested, expected phase diagram of the section $NaNdP_2O_7$–$NaNd(PO_3)_4$ is shown in the upper-left corner of the figure. To propose an exact diagram was not possible for the following reasons. (i) Liquidus curves could not be drawn, because the DTA-heating curves have not shown any effects connected with the melting of the samples. (ii) DTA curves reveal only a single, very strong endothermic effect in the $NaNdP_2O_7$--rich part of the system (*i.e.* for samples, containing less than 28 wt. % $NaNd(PO_3)_4$), which hindered an exact identifying of the composition at point „c" (see Figs. 3 and 4).

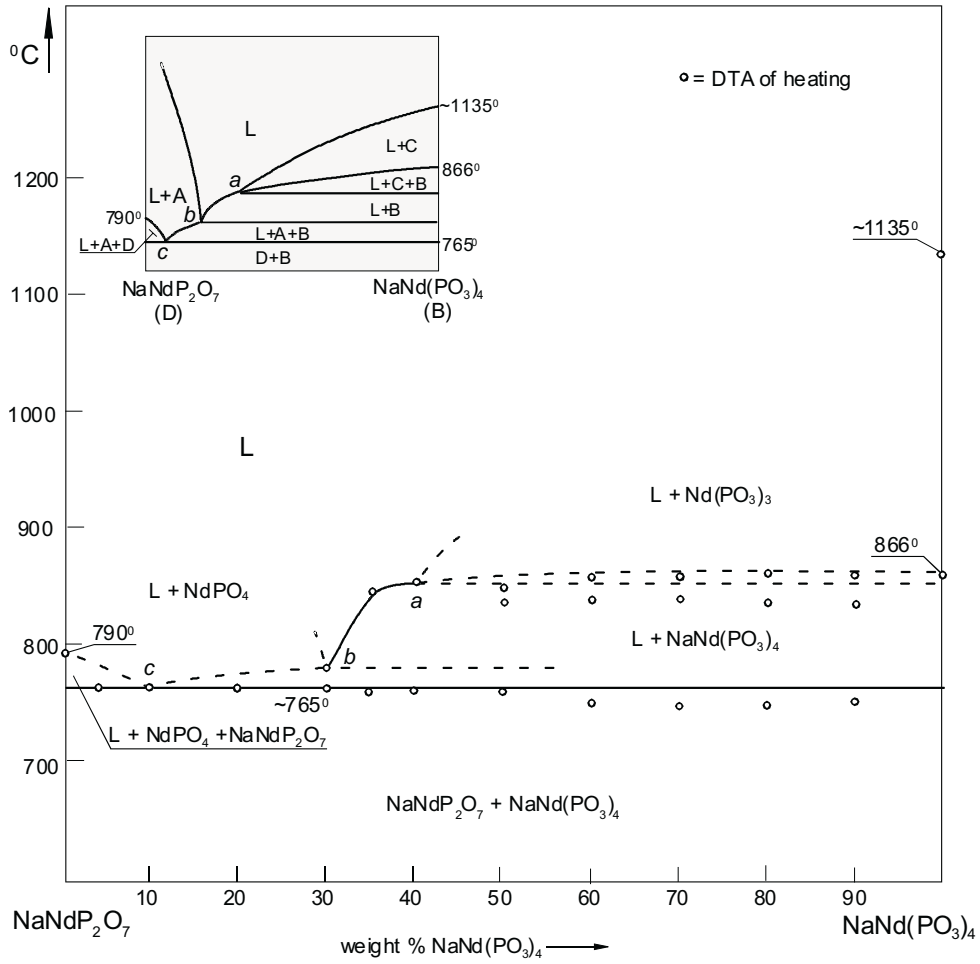


**Figure 3.** Phase relations in the quasi-binary section $NaNdP_2O_7$–$NaNd(PO_3)_4$.

Fig. 4 shows a phase diagram of the partial system $NdPO_4$–$Nd(PO_3)_3$–$NaPO_3$. In this triangle, two phases ($NaNdP_2O_7$ and $NaNd(PO_3)_4$) are formed as a result of peritectic reactions, proceeding in the side systems. A peritectic reaction in the side system $Nd(PO_3)_3$–$NaPO_3$ proceeds at 866°C and gives $NaNd(PO_3)_4$ phosphate. Another such reaction occurs in the side system $NdPO_4$–$NaPO_3$ at 790°C, giving $NaNdP_2O_7$ phosphate. Peritectic reactions, proceeding in side systems, manifest in the ternary partial system in the form of two ternary peritectic reactions. In the region $NdPO_4$–$P_1$–$NaNd(PO_3)_4$–$Nd(PO_3)_3$ (*i.e.* triple peritectic quadrangle) the ternary peritectic reaction occurs, that proceeds at about 850 ºC, according to the network: $Nd(PO_3)_3 + L_{P_1} \rightarrow NdPO_4 + NaNd(PO_3)_4$. Next, in the region determined by the points

$NdPO_4$–$NaNdP_2O_7$–$P_2$–$NaNd(PO_3)_4$ (*i.e.* another triple peritectic quadrangle), a ternary peritectic reaction occurs, that proceeds at about 765 °C, according to the network: $NdPO_4 + L_{P_2} \rightarrow NaNdP_2O_7 + NaNd(PO_3)_4$.

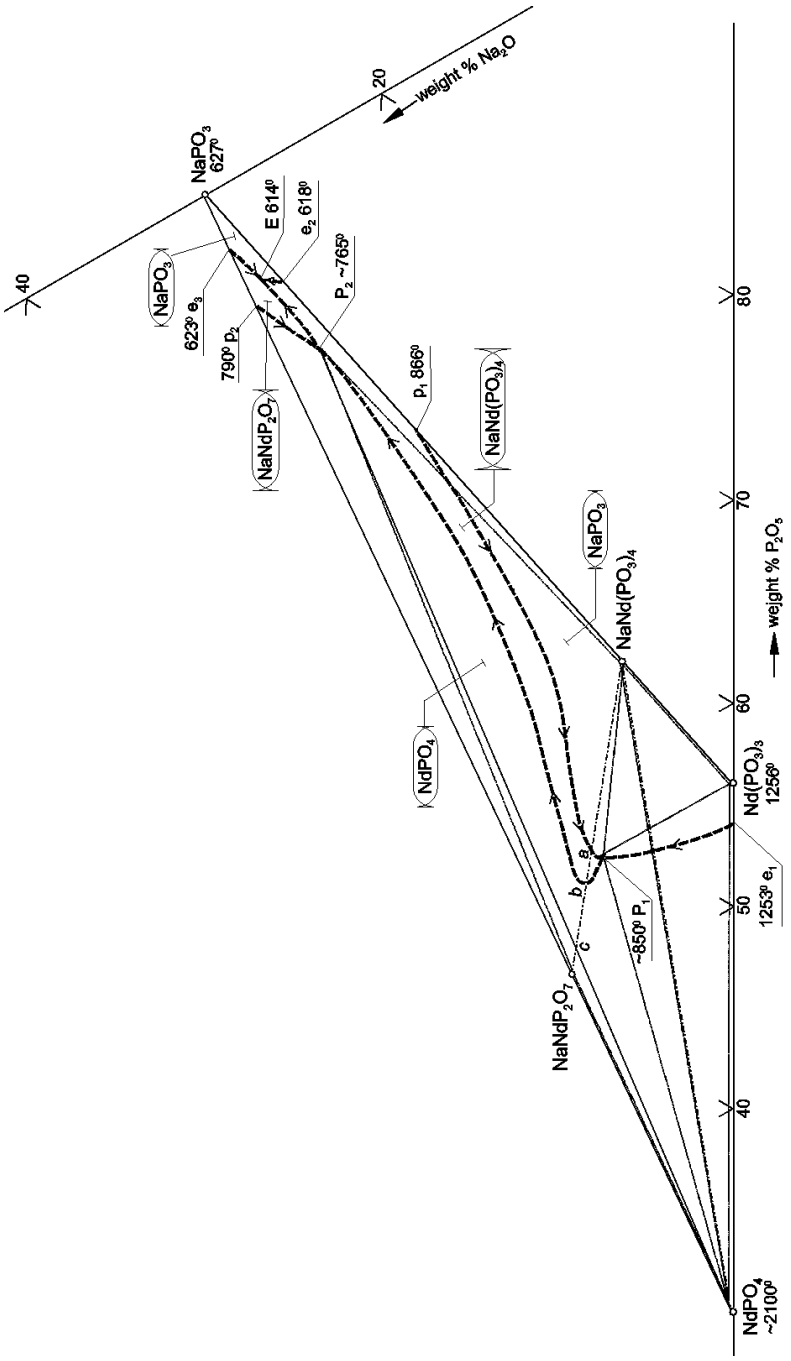


**Figure 4.** Phase diagram of $NdPO_4$–$NaPO_3$–$Nd(PO_3)_3$ system.

A ternary eutectic E occurs in the partial system, and it melts at a constant temperature of 614°C. There are five regions of the primary crystallization of binary and ternary compounds in the composition range under investigation. The regions are bounded by eutectic and peritectic curves. In Fig. 4 these regions are drawn by a dashed line, because their form and location are approximate, as a result of the approximate character of the phase diagrams of Figs. 2 and 3. It should be noted, that during the experimental work the adaptation of DTA-cooling was impossible (related to complicate processes of the phosphates: $NaNdP_2O_7$ and $NaNd(PO_3)_4$).

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