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# Phase Equilibria in the System $Nd(PO_3)_3$ – $KPO_3$

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The system $Nd(PO_3)_3$ – $KPO_3$ has been investigated by differential thermal analysis (during heating), thermogravimetric analysis, mass spectrometry, Raman spectroscopy and X-ray powder diffraction and its phase diagram was proposed. It was discovered that initial metaphosphates react at a 1:1 molar ratio forming intermediate compound $KNd(PO_3)_4$. It was found that it melts incongruently at 854°C giving $Nd(PO_3)_3$ and a liquid rich in $KPO_3$. Phosphate $KNd(PO_3)_4$ is stable down to room temperature and does not show any polymorphic transitions.

**Key words**: phase diagram, DTA, X-ray, neodymium-potassium metaphosphate

Investigations of phase equilibria in the ternary systems $Ln_2O_3$–$M^I_2O\{M^{II}O\}$–$P_2O_5$, where Ln = rare earth element and Y, $M^I$ = alkali metal, $M^{II}$ = alkaline earth metal, are carried out in this laboratory for over ten years. Our interest in compounds of these systems is due to their well-known application aspects. As part of our continued work on the above systems, we started a study of unknown, so far, phase equilibria in the system $Nd_2O_3$–$K_2O$–$P_2O_5$. In this paper the results of the phase investigation of the binary section $Nd(PO_3)_3$–$KPO_3$ are described.

According to [1], neodymium metaphosphate $Nd(PO_3)_3$ crystallizes in the orthorhombic system, space group $C222_1$ with unit cell parameters $a = 11.172$, $b = 8.533$, $c = 7.284$ Å. Metaphosphate $KPO_3$ melts congruently at 810°C and begins to decompose at about 1160°C (in the liquid phase). The decomposition is accompanied by a slow mass decrement. For $KPO_3$ the existence of two polymorphic forms with the transition at 449°C has been confirmed and its third polymorphic form has been found within the temperature range 665–810°C [2,3]. According to [4], the metaphosphate $KPO_3$ crystallizes in the monoclinic system with unit cell parameters $a = 11.074(8)$, $b = 11.965(9)$, $c = 7.350(6)$ Å, $\beta = 102.18°$.

Also known is the double metaphosphate $KNd(PO_3)_4$. Its crystal structure, as a new high – Nd-concentration laser material, was reported in [5]. $KNd(PO_3)_4$ crystallizes in the monoclinic system, space group $P2_1$ and has cell parameters $a = 7.266(1)$, $b = 8.436(1)$, $c = 8.007(1)$, $\beta = 91.97(1)°$.

## EXPERIMENTAL

Specimens of the binary system $Nd(PO_3)_3$–$KPO_3$ were prepared from the initial metaphosphates. The compounds were prepared from the ready – made reagents: $Nd_2O_3$ (99.99%), $H_3PO_4$ (85%), $K_2HPO_4$ and $(NH_4)_2HPO_4$ – all analytically pure.

$KPO_3$ was obtained from $KH_2PO_4$ by heating at 350°C for 2 h (by completely dehydrating). $Nd(PO_3)_3$ was obtained from $NdPO_4$ and $(NH_4)_2HPO_4$. These substrates, mixed in the molar ratio 1:2, were heated in a platinum crucible at 100°C for 1 h, at 200°C for 2 h, at 400°C for 2 h and 900°C for 24 h. Orthophosphate $NdPO_4$ was obtained from the following solution: 0.4 wt% of $Nd_2O_3$, 15 wt% of $P_2O_5$ (as $H_3PO_4$), 84.6 wt% of distilled water. The mixture was placed in a round-bottomed flask, brought to a boil in a reflux condenser, and held there for 6 h. The precipitated $NdPO_4$ was filtered, washed several times with hot distilled water, dried at 200°C and sintered at 900°C for 1 h.

The specimens for phase investigation in the binary system $Nd(PO_3)_3$–$KPO_3$ were presynthesized by solid state reactions. The conditions for the synthesis were established through initial experiments carried out to determine the parameters necessary for attaining the equilibrium state of a specimen. Specimens composed in initial mixtures of up to 40 wt % $KPO_3$ (in terms of the system components) were sintered at 750°C for 5 h. In the other range of component concentration the specimens were sintered at 600° for 8 h.

The phase investigations were performed by differential thermal analysis (DTA) during heating, thermogravimetric analysis (DTG), mass spectrometry, Raman spectroscopy and powder X-ray diffraction. The initial experiments showed that the specimens of the system under investigation hardly crystallized and strongly tended to set vitrified. A visual evaluation was employed in the case of specimens, whose melting point could not be determined from the DTA of heating (because of the lack of thermal effects in the high temperetaure DTA curves). Specimens for the visual evaluation were prepared as follows. The parent metaphosphates were weighed out in fixed amounts, mixed carefully and ground in an agate mortar, then pressed into pellets and presynthesized with intermediate remixings by sintering. The visual observation consisted in taking notes of the temperature at which the specimen liquified and the temperature at which it became transparent. Hence, the temperatures are treated as approximate. The visual observations were carried out using a home made resistance furnace with a Pt30Rh [6]. DTA of heating was performed by a derivatograph Type 3427 (MOM, Hungary) over the range 20–1350°C with the heating rate 5°/min. Platinum crucibles in air atmosphere and specimens of weight 0.2–0.7 g were used. The standard substance was high-purity $Al_2O_3$. Temperature was read by a Pt/Pt10Rh thermocouple, which was calibrated against the melting points of NaCl and $K_2SO_4$ and the polymorphic transition temperature of $K_2SO_4$ (583°C). Additionally, the thermal analysis combined with mass spectrometry of the gas phase was applied. This investigation was made by using a derivatograph of the type STA 409C (Netzsch) and a ThermoStar GSD 300T spectrometer (Balzers Instruments). The Raman spectra were obtained using Fourier Transform Bruker 100S spectrometer.

The phase purity of the substances was determined and the phases in the binary system were identified by powder X-ray diffraction. Siemens diffractometers D 5000 and HZG-4 (B-TUR M 62) with CuK$\alpha$ radiation and a Ni – filter were used.

## RESULTS AND DISCUSSION

The phase equilibria in the system $Nd(PO_3)_3$–$KPO_3$ were determined over the whole composition and temperature ranges by DTA and DTG, mass spectrometry, Raman spectroscopy and powder X-ray diffraction. Heating the specimens of the system, the TG curves indicate a mass loss. The temperature corresponding to the onset of the effect was dependent on the composition of the specimen under investigation. For $Nd(PO_3)_3$ – rich specimens a slow, gradual mass loss started at 1080°C. With increasing $KPO_3$ content, the temperature for this mass loss onset increased to the maximum about 1160°C. It was necessary to elucidate this interesting effect.

In the $KPO_3$ – rich part of the system, the mass loss is the result of metaphosphate $KPO_3$ decomposition. According to earlier investigations, pure $KPO_3$ begins to decompose at about 1160°C (in the liquid phase). This observation inclined the authors to investigate, in turn, the thermal stability of the $Nd(PO_3)_3$ and check its melting point. Lanthanide metaphosphates, $Ln(PO_3)_3$, are known to be thermally unstable. According to [7,8], they decompose to the corresponding orthophosphate (*i.e.* $LnPO_4$) with evolution of $P_2O_5$. Thermogravimetric analysis of $Nd(PO_3)_3$ showed in turn that about 1080°C (in the solid phase) a slow, gradual weight loss began. In order to find the origin of this effect, an isothermal examination of the compound mass loss was carried out at the 1080°C. It was found that the 25 hours mass loss was 18.1%. The phase composition of the resultant product (sinter) was checked by powder X-ray analysis. X-ray diffractogram showed only reflections typical of $Nd(PO_3)_3$. The above results indicated that the mass loss was not connected with $Nd(PO_3)_3$ decomposition and the evolution of $P_2O_5$. To verify this conclusion, thermal analysis combined with mass spectrometry of the gas phase was employed. In this examination a specimen of the $Nd(PO_3)_3$ metaphosphate was heated at 1080°C for 6 hours. Such prolonged heating resulted in a mass loss of only 1.2%. The accompanying analysis of the gas phase did not show any evidence of $P_2O_5$. The FT Raman spectra of the samples, as synthesized and heated at 1080°C for 25 h were compared, *i.e.* before and after the temperature, in which the weight loss appears. They exhibit two multiplets of a very strong intensity at about 1070 and 1340 nm, which correspond to the $^4F_{3/2} \rightarrow {}^4I_{11/2}$ and $^4F_{3/2} \rightarrow {}^4I_{13/2}$ emission transitions of the $Nd^{3+}$ ion, respectively. In the range 500–1300 $cm^{-1}$ the Raman spectra of both samples can be seen. They consist of several lines connected with the bending and stretching vibrations of the $PO_3^-$ ion. The spectra of both samples are the same, both in respect of number and energetic position of all spectral multiplets. It means that the temperature anomaly at 1080°C does not change the composition and structure of the sample. Finally, it was admitted that the mass loss, which was observed during heating the specimens of the $Nd(PO_3)_3$–$KPO_3$ system, did not affect the equilibrium state under conditions of the present experiment.

The next problem to be elucidated was whether the system $Nd(PO_3)_3$–$KPO_3$ would yield a phosphate of the formula $KNd(PO_3)_4$. This double phosphate with its molar ratio $Nd(PO_3)_3$:$KPO_3$ = 1:1 (76.35 wt% $Nd(PO_3)_3$, 23.65 wt% $KPO_3$) should be an intermediate compound in the binary system under investigation. To verify this hypothesis, an equimolar mixture of metaphosphates mentioned above was heated at different temperatures for different times. Phase composition of the sinters obtained was every time controlled by roentgenography. Finally, it was found that $KNd(PO_3)_4$ can be achieved *via* the solid state reaction by heating the equimolar mixture of the metaphosphates $Nd(PO_3)_3$ and $KPO_3$ at 750°C for 5 h. In this way it was proved that $KNd(PO_3)_4$ appears as an intermediate compound in the binary system of interest. Based on DTA during heating, it was found that $KNd(PO_3)_4$ melts incongruently at 854°C to give $Nd(PO_3)_3$ and a $KPO_3$-rich liquid. The compound is thermally stable down to room temperature and does not exhibit polymorphic transitions.

The last stage of investigation was the construction the phase diagram of the $Nd(PO_3)_3$–$KPO_3$ system. It is shown in Fig. 1. Determining the liquidus and solidus curves in certain composition ranges was rather difficult. Thermal effects connected with melting were clearly seen mainly on DTA-heating curves of $KPO_3$ – rich specimens, while such effects in other ranges of composition were diffuse (which made the melting point of the specimen difficult to determine). In such cases the visual evaluation was used. For this reason the liquidus curve, in some ranges of composition, has been drawn by a dashed line. Another problem was linked to determining the melting point and composition of the eutectic mixture. It results from Fig. 1 that at the lowest temperature, 678°C, a specimen of the content 67.5 wt % $KPO_3$ melts. Almost at the same temperature a thermal effect appears on the DTA-heating curve for a specimen of the content 65 wt % $KPO_3$ (35 wt % $Nd(PO_3)_3$). In contrast, the DTA-heating curves of the remaining specimens, *i.e.* of the composition between 60 and 95 wt % $KPO_3$, the thermal effect linked to the melting of eutectic was seen at temperatures higher by about 20°C.

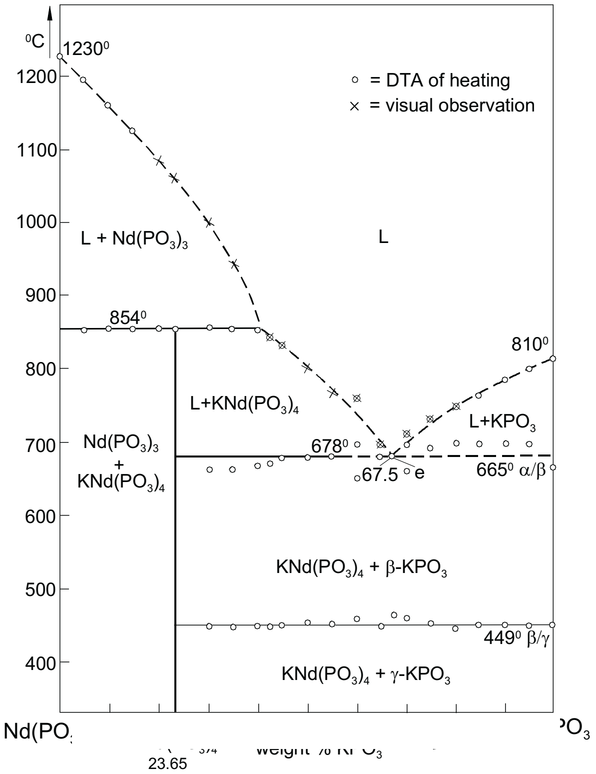

Fig 1. Phase relations in the $Nd(PO_3)_3$ - $KPO_3$ system.

**Figure 1.** Phase relations in the $Nd(PO_3)_3$–$KPO_3$ system.

In view of the anomalies described above, the DTA of heating were several times repeated for specimens of the composition between 60 and 95 wt % $KPO_3$. The result was similar each time. Finally, the composition and temperature of eutectic point was assumed to be: 67.5 wt % $KPO_3$, 32.5 wt % $Nd(PO_3)_3$; and 678°C. Hence, the solidus curve in the $KPO_3$ – rich part has been drawn by a dashed line. In the high temperature part of the system $Nd(PO_3)_3$–$KPO_3$, in the composition range 0–41 wt % $KPO_3$, a peritectic reaction takes place. It proceeds according to $KNd(PO_3)_4 \rightarrow Nd(PO_3)_3 +$ liquid.

The phosphate $KPO_3$ appears in three polymorphic modifications. In the composition range 30–100 wt % $KPO_3$ the low temperature transition $\beta/\gamma$-$KPO_3$ is observed in the form of clear thermal effects on the curves of DTA-heating. However, the high-temperature transition $\alpha/\beta$-$KPO_3$ and the eutectic yield probably a single common thermal effect on the DTA-heating curves.

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