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Phase Equilibria in the Ternary System Nd_2O_3–K_2O–P_2O_5. The partial system $NdPO_4$–KPO_3–$Nd(PO_3)_3$

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In the ternary system Nd_2O_3–K_2O–P_2O_5 a partial system $NdPO_4$–KPO_3–$Nd(PO_3)_3$ was investigated by thermoanalytical methods, X-ray powder diffraction and microscopy in reflected light and its phase diagram was proposed. In the system a double metaphosphate $KNd(PO_3)_4$ appears. The compound forms in a side system $Nd(PO_3)_3$–KPO_3. It has been established that the $KNd(PO_3)_4$ and $NdPO_4$ form a section, which is a real system only in the subsolidus region. It is found, that a ternary peritectic ($t_P \sim 885°C$) and a ternary eutectic ($t_E \sim 688°C$) occur in the partial system $NdPO_4$–KPO_3–$Nd(PO_3)_3$.

Key words: phase diagram, DTA, TG, DTG, X-ray, neodymium-potassium phosphates

Steady interest in rare earth element and yttrium phosphates is connected with their possible application as laser materials, luminophores and others. Accordingly, within the framework of our long-term research of multicomponent phosphates, an attempt was made to establish phase equilibria of the ternary system Nd_2O_3–K_2O–P_2O_5. Phase diagrams of its side systems are known. The phase diagram of the basic side system Nd_2O_3–P_2O_5 was worked to the temperature 1500°C [1]. These authors have identified six neodymium phosphates of the formulae NdP_5O_{14}, $Nd(PO_3)_3$, $Nd_2P_4O_{13}$, $NdPO_4$, Nd_3PO_7 and $Nd_7P_3O_{18}$. Another side system, K_2O–P_2O_5, is described in some papers [2–7]. In this system four intermediate compounds: KPO_3, $K_5P_3O_{10}$, $K_4P_2O_7$ and K_3PO_4 have been identified.

In our own studies of the system Nd_2O_3–K_2O–P_2O_5 we found the existence of the section $Nd(PO_3)_3$–KPO_3 and presented its phase diagram. For this section we have observed the appearance of the binary phosphate $KNd(PO_3)_4$, which melts incongruently at 889°C giving $Nd(PO_3)_3$ and a KPO_3-rich liquid. The compound is stable at room temperature. The system includes an eutectic of the parameters: 65 wt. % of KPO_3, 35 wt. % $Nd(PO_3)_3$, melting point 690°C. In this paper we present the results of the investigation of the Nd_2O_3–K_2O–P_2O_5 system, which has been extended to the P_2O_5-rich area, *i.e.* in the composition range $NdPO_4$–KPO_3–$Nd(PO_3)_3$.

EXPERIMENTAL

Samples were prepared from ready-made reagents and in-house obtained phosphates. The following ready-made reagents were used: Nd_2O_3 (99.99%), H_3PO_4 (85%), $(NH_4)_2HPO_4$ and KH_2PO_4, all analytically pure. Potassium metaphosphate KPO_3 was obtained by complete dehydrating of KH_2PO_4 at 350°C for 2 h. Neodymium metaphosphate $Nd(PO_3)_3$ was synthesized from Nd_2O_3 and $(NH_4)_2HPO_4$ *via* a solid-state reaction. These substrates, mixed in the molar ratio 1:6, were thoroughly rubbed in an agate mortar to attain homogeneity. Then the mixture was sintered in the following three stages: (i) 450°C for 28 h to expel NH_3 and H_2O; (ii) 900°C for 26 h; (iii) 1050°C for 26 h. After each stage the sinter was thoroughly ground and mixed. 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 boiling 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. Double phosphate $KNd(PO_3)_4$ was obtained by the solid-state reaction *via* heating an equimolar mixture of $Nd(PO_3)_3$ and KPO_3 at 750°C for 10 h. The investigations of the phase equilibria in the partial system $NdPO_4$–KPO_3–$Nd(PO_3)_3$ were performed by thermoanalytical methods (DTA, TG, DTG), microscopy in reflected light and X-ray powder diffraction. The samples for investigations were presynthesized by solid-state reaction. The substrates were weighed out in fixed amounts, thoroughly mixed in agate mortar and then sintered. The sintering temperature and the time in relation to the composition of the samples were determined experimentally. The thermoanalytical investigations were performed by using a calorimeter type SETSYS™ (TG – DSC; SETARAM) up to 1400°C (scanning rate 10 $K\cdot min^{-1}$), under argon, platinum crucibles; weight of samples was 0.001 to 0.020 g. 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). The visual observations were carried out using a home-made resistance furnace with a PtRh 30 winding. High-temperature thermal studies (above 1400°C) were performed in a horizontal resistance furnace of our construction with molybdenum winding or wolfram pipes under argon. The presynthesized samples were pressed into pellets. Temperature was read by an optical pyrometer, which was calibrated against the melting points of $Ca_3(PO_4)_2$ and Na_3PO_4. The phase purity of reagents and phase structure of the products were studied microscopically in reflected light. Microsections, that were polished and examined by microscopy in reflected light, were prepared from molten and crystallized samples.The phase purity of the reagents was determined and the phases in the partial system were identified by X-ray powder diffraction. Siemens diffractometer D 5000 and HZG 4 (B-TUR M 62) with CuK_α radiation were used.

RESULTS AND DISCUSSION

Phase equilibria, that occur in the ternary partial system $NdPO_4$–KPO_3–$Nd(PO_3)_3$, have been investigated in the entire range of composition, up to 1800 °C by DTA, TG, DTG, X-ray powder diffraction and light microscopy. The above partial system is surrounded by three side systems: (i) $NdPO_4$–$Nd(PO_3)_3$, (ii) $Nd(PO_3)_3$–KPO_3 and (iii) $NdPO_4$–KPO_3. Phase diagrams of the first two systems are known. According to [1], the $NdPO_4$ and $Nd(PO_3)_3$ phosphates give a simple eutectic system. However, the composition of the eutectic point is not given and the liquidus curve, marked by a dashed line, gives the melting points uncertain for the samples of the $NdPO_4$–$Nd(PO_3)_3$ system. The phase equilibria concerning the third side system, $NdPO_4$–KPO_3, have not been reported so far.

In view of the above, investigation of the phase equilibria occurring in the composition range $NdPO_4$–KPO_3–$Nd(PO_3)_3$ was started from determination of parameters of eutectic-point, which exists in the $NdPO_4$–$Nd(PO_3)_3$ system. We found that the eutectic mixture has a composition of 92.5 wt. % $Nd(PO_3)_3$ and 7.5 wt. % $NdPO_4$; it melts at 1253°C. The data of the eutectic point are necessary for drawing the curve

e_1P that corresponds to liberation of the binary eutectic (see Fig. 2). Melting point of $NdPO_4$ orthophosphate, determined by the horizontal resistance furnace, amounts to about 2100°C.

In order to establish the phase diagram of the $NdPO_4$–KPO_3 system, the experiment was begun with checking the existence of diphosphate $KNdP_2O_7$. According to literature, there were known double phosphates of an overall formula of $M^IM^{III}P_2O_7$ (where M^I = Na, K, Rb, Cs,...; M^{III} = Y and certain rare-earth elements). It should be noted, however, that potassium produces diphosphates only with M^{III} = Tb – Lu (Ref. [8]), which does not include the compound $KNdP_2O_7$. As this empirical formula implies the molar ratio of $NdPO_4$:KPO_3 to 1:1, it was reasonable to expect the appearance of such a phosphate in the system $NdPO_4$–KPO_3. Therefore, it was useful to examine the supposition based on the information in [8]. Consequently, an equimolar mixture of $NdPO_4$ and KPO_3 phosphates was heated in the solid phase at different temperatures and using different sintering times. The phase composition of all sinters obtained was identified by X-ray powder diffraction. It was found that irrespective of the time and temperature applied, the sinters obtained were a mixture of $NdPO_4$ and KPO_3 phosphates. Based on this result, the lack of an intermediate compound of the formula $KNdP_2O_7$ was assumed to be meaningful for the system $NdPO_4$–KPO_3. To examine phase equilibria characteristic of the above system, samples of heteromolar mixtures of the parent phosphates were presynthesized by the solid state reaction. The temperature and time of the presynthesis were dependent on sample composition. KPO_3-rich samples were heated at 750°C for 10 h, whereas those $NdPO_4$-rich were at 850°C for 15 h.

The phase diagram in Fig. 1 for the $NdPO_4$–KPO_3 system is proposed on the basis of the results obtained by thermoanalytical investigations, phase X-ray powder diffraction and observation of polished sections by light microscopy. The system is found to be a simple eutectic. The eutectic-point parameters are: 97.5 wt. % KPO_3 and 2.5 wt. % $NdPO_4$; melting point about 795°C. Samples of composition close to that of the eutectic point demonstrate the eutectic phase transformation in a certain range of temperature. On DTA-heating curves this is manifested by two subsequent endothermic effects. To interpret this phenomenon, observation of microsections in reflected light was helpful. An overall conclusion arises that the melted KPO_3-rich samples crystallize with the segregation process occurring, which means the lack of a perfect homogenization of composition. The segregation is probably the result of a quite big difference in melting point between the parent phosphates ($NdPO_4$ and KPO_3), as well as the known tendency of the metaphosphate KPO_3 to solidify in the form of glass. It should be also mentioned, that either no effects are present on the DTA-heating curves (which is in contrast to what has been observed for most of the melted samples) or such effects can be noticed as faint and diffuse. Establishing the exact shape of the liquidus curve in the entire composition range appears to be practically not possible. Part of the curve is, therefore, drawn by a dashed line on the diagram. Pure metaphosphate KPO_3 occurs in three polymorphic modifications. Transition points are 665°C for the α/β and 449°C for the β/γ. The transformations

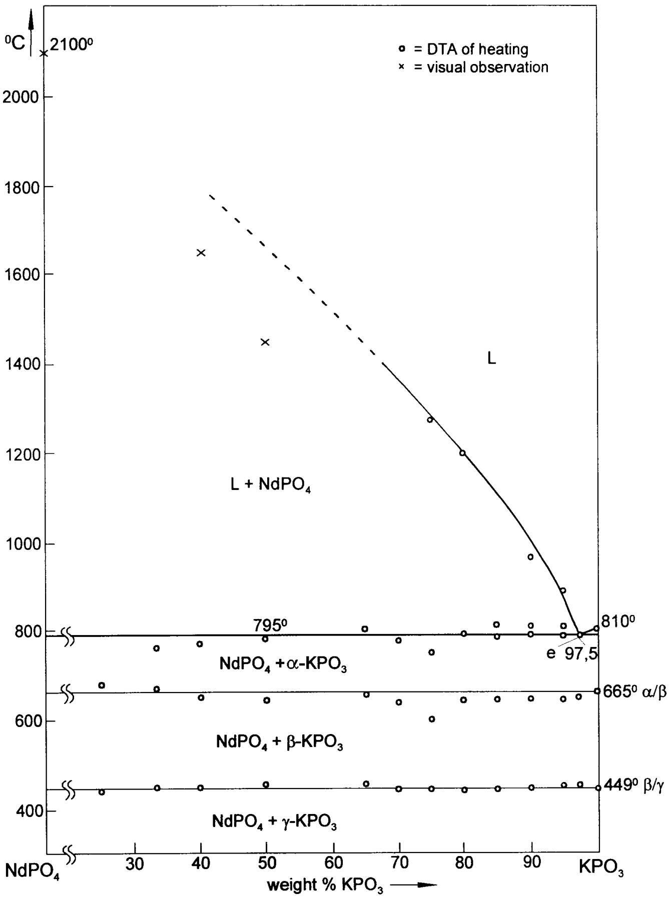

Figure 1. Phase relations in the $NdPO_4$–KPO_3 system.

manifest on the DTA-heating curves, in the entire range of composition of the system $NdPO_4$–KPO_3, as clear endothermic effects.

The final stage of this work was to establish the phase equilibria that occur in the ternary partial system $NdPO_4$–KPO_3–$Nd(PO_3)_3$. Initial X-ray powder diffraction tests revealed the existence of the $NdPO_4$–$KNd(PO_3)_4$ section in this range. The samples for this section were synthesized from the initial phosphates *via* the solid state reaction, whereby the presynthesis was a heating at 600°C for 24 h. Heteromolar mixtures of $NdPO_4$ and $KNd(PO_3)_4$ were presynthesized and subjected to DTA of heating. A single, strong endothermic effect was revealed on the DTA-heating curves at about 885°C. During the course of heating, also a loss of mass was noted on the TG curves, at about 1100°C. In order to elucidate this phenomenon, some samples of the system in question were melted, which was followed by cooling with grafting to room temperature to cause crystallization. The phase composition of the samples, obtained in this way, was identified by X-ray powder diffraction. Diffraction patterns displayed reflections typical of $Nd(PO_3)_3$, $NdPO_4$ and traces of KPO_3. Therefore, the loss of mass could be clearly linked to a change in the initial composition of samples. Also complementary, visual observations were carried out. The procedure was as follows: presynthesized samples were pressed into pellets and placed into a platinum crucible to be treated by heating in a vertical furnace. The temperature, at which the sample got soft and diffuse, was recorded. In that way the onset of melting was found to appear at about 880°C. The phase diagram of the $NdPO_4$–$KNd(PO_3)_4$ section could not be constructed on the above data. A theoretical consideration leads to the conclusion that this section cannot have all features of a quasi-binary system, in spite of that it is bounded on one side by the orthophosphate $NdPO_4$ (which melts congruently) and on the other side by the peritectic $KNd(PO_3)_4$. It should be then a real (quasi-binary) system only in the sub-solidus region, *i.e.* below 885°C. Hence, the high-temperature region of this section has a multiphase character. The above consideration is confirmed by the presence of thermal effects on the DTA-heating curves of presynthesized samples of the partial system $NdPO_4$–KPO_3–$Nd(PO_3)_3$. Owing to those effects it can be established that the ternary peritectic P, that occurs in the partial system of interest, melts at 885°C.

Phase diagram of the $NdPO_4$–KPO_3–$Nd(PO_3)_3$ partial system is shown in Fig. 2. The section $NdPO_4$–$KNd(PO_3)_4$, described above, divides the partial system of interest into two triangles: (i) $NdPO_4$–$KNd(PO_3)_4$–$Nd(PO_3)_3$ and (ii) $NdPO_4$–KPO_3–$KNd(PO_3)_4$. These differ in crystallization run and in their end temperature of solidification. There occur four compounds in this system, which crystallize from

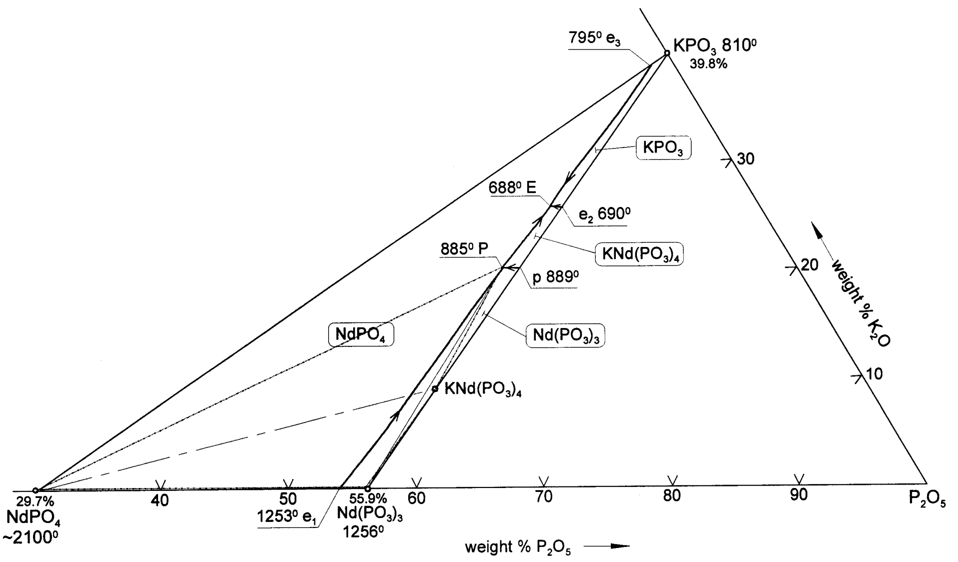

Figure 2. The partial system $NdPO_4$–KPO_3–$Nd(PO_3)_3$.

the liquid phase: $NdPO_4$, $Nd(PO_3)_3$, KPO_3 and $KNd(PO_3)_4$. Double metaphosphate $KNd(PO_3)_4$ forms in a side system $Nd(PO_3)_3 - KPO_3$, according to the reaction: $L_p + Nd(PO_3)_3 \rightarrow KNd(PO_3)_4$, where L_p – denotes a liquid of composition as in point p. According to, pP – curve corresponds to liberation of the binary peritectic, which proceeds as: $L_{pP} + Nd(PO_3)_3 \rightarrow KNd(PO_3)_4$, ($L_{pP}$ denotes a liquid with a composition corresponding to the points in the line pP).

During solidification of the mixtures of composition corresponding to those of the points of the field $NdPO_4$–P–$KNd(PO_3)_4$–$Nd(PO_3)_3$ (*i.e.* the triple peritectic quadrangle) there proceeds the ternary peritectic reaction: $L_P + Nd(PO_3)_3 \rightarrow NdPO_4 + KNd(PO_3)_4$, (where L_P denotes a liquid of composition as in point P). The reaction proceeds at a constant temperature of about 885°C. The latter is the solidification point of the alloys of composition, corresponding to points of the field $NdPO_4$–$KNd(PO_3)_4$–$Nd(PO_3)_3$. As the result of the peritectic reaction mentioned above, in the alloys of the field $NdPO_4$–P–$KNd(PO_3)_4$ an excess liquid L_P remains. Therefore, solidification of those alloys does not finish at 885°C. The solidification proceeds along line PE at a diffuse temperature (from 885 to 688°C) and consists in separating of the binary eutectic ($NdPO_4$ + $KNd(PO_3)_4$). Upon reaching point E, the ternary eutectic reaction starts at a constant temperature of about 688°C. At this point the alloys' solidification ends with liberation of the ternary eutectic ($NdPO_4$ + KPO_3 + $KNd(PO_3)_4$).

According to Fig. 2 the orthophosphate $NdPO_4$ occupies the largest field of primary crystallization. This includes the entire range of composition: $NdPO_4$-e_3-E-P-e_1. The fields of the primary crystallization of the remaining phosphates are quite small and cover the following composition ranges: (i) potassium metaphosphate: the field e_2-E-e_3-KPO_3, (ii) double metaphosphate $KNd(PO_3)_4$: the field p-P-E-e_2, (iii) neodymium metaphosphate: the field $Nd(PO_3)_3$-e_1-P-p.

During the establishing the phase equilibria in the partial system $NdPO_4$–KPO_3–$Nd(PO_3)_3$ several serious difficulties appeared. The main problems were: (i) quite a big difference in melting points between the samples from 2100°C (in the $NdPO_4$-rich part of the system) up to about 680°C (for the samples located near points E and P), see Fig. 2, (ii) lack of melting-originated thermal effects on the DTA-heating curves, which was the case in most samples, (iii) tendency of the melted, KPO_3-rich samples to solidify as glasses.

REFERENCES

1. Wong M-S. and Kreidler E.R., *J. Am. Ceram. Soc.,* **70(6)**, 396 (1987).
2. Parravano N. and Calcagni G., *Z. anorg. Chem.,* **65**, 1 (1910).
3. Morey G.W., *J. Am. Ceram. Soc.,* **76**, 4724 (1954).
4. Bergman A.G. and Sanzharova Z.I., *Zh. Neorg. Khim.,* **14**, 1 (1969).
5. Znamierowska T., *Polish J. Chem.,* **52**, 1889 (1978).
6. Belyaev I. and Sigida N.P., *Zh. Neorg. Khim.,* **3**, 425 (1958).
7. Znamierowska T., *Polish J. Chem.,* **55**, 747 (1981).
8. Anisimowa N.J., Czudinowa N.N. and Trunow W.K., *Neorg. Materiały,* **29(1)**, 105 (1993).