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Study of Phase Equilibria in the System Nd_2O_3–Na_2O–P_2O_5. The Quasi-Binary Section $Nd(PO_3)_3$–$NaPO_3$

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The quasi-binary section $Nd(PO_3)_3$–$NaPO_3$ has been investigated by thermoanalytical methods (DTA, TG, DTG) and X-ray powder diffraction and its phase diagram was proposed. It was found that initial metaphosphates react at a 1:1 molar ratio, forming the intermediate compound $NaNd(PO_3)_4$. It was confirmed, that it melts incongruently at about 866°C, giving $Nd(PO_3)_3$ and a liquid rich in $NaPO_3$. The phosphate $NaNd(PO_3)_4$ is stable to room temperature and does not exhibit polymorphic transitions.

Key words: phase diagram, DTA, TG, DTG, X-ray, sodium-neodymium metaphosphate

Phosphates of rare earth elements, as well as those doped with different elements, are known to be of practical interest as laser materials, luminophores *etc*. Work to establish phase diagrams of ternary systems of the type Ln_2O_3–$M^I_2O(M^{II}O)$–P_2O_5, (where Ln is a lanthanide element or yttrium, M^I is an alkali metal and M^{II} is an alkaline earth metal) is being performed in our laboratory for many years. It gives the possibility to identify unknown phases for technological application. In this paper we present results of an investigation of the ternary system Nd_2O_3–Na_2O–P_2O_5 in the P_2O_5-rich area. It has been found that a quasi-binary section $Nd(PO_3)_3$–$NaPO_3$ exists, whose phase diagram was not known before. Some literature information covers the parent metaphosphates, $Nd(PO_3)_3$ and $NaPO_3$. The method of obtaining $Nd(PO_3)_3$ compound was given, among others, in [1,2]. We have examined thermal stability of the compound. According to [1], $Nd(PO_3)_3$ phosphate melts congruently at 1280±5°C and does not reveal any polymorphic transformation. It crystallizes in orthorhombic system; space group $C222_1$; lattice parameters $a = 11.172$, $b = 8.533$, $c = 7.284$ Å, [3]. $NaPO_3$ metaphosphate melts congruently at 627°C and appears in three polymorphic modifications. The transitions occur at 510°C for α/β and 404°C for β/γ [4]. Thermal stability of the metaphosphate is described in [5]. According to [6], the compound $NaPO_3$ may crystallize in monoclinic system, space group $P2_1/n$ or in orthorhombic system, space group *Pmcn.* A binary metaphosphate $NaNd(PO_3)_4$ is known, too. We could observe it as an intermediate compound in the system $Nd(PO_3)_3$–$NaPO_3$ with the molar ratio 1:1 of parent metaphosphates. The phosphate $NaNd(PO_3)_4$ crystallizes in monoclinic system; space group $P2_1/n$; lattice parameters $a = 9.907(4)$, $b = 13.10(1)$, $c = 7.201(3)$ Å, $\beta = 90.51(3)°$ [7].

EXPERIMENTAL

Samples for investigation of the section $Nd(PO_3)_3$–$NaPO_3$ were synthesized mostly from parent metaphosphates by solid-phase reaction. The metaphosphates were home made by using the commercial reagents: Nd_2O_3 (99.99%), $NaH_2PO_4\cdot H_2O$, $(NH_4)_2HPO_4$ – all analytically pure. Sodium metaphosphate $NaPO_3$ was obtained by a complete dehydratation of $NaH_2PO_4\cdot H_2O$ for 1 h at 300°C and 1 h at 500°C. Neodymium metaphosphate $Nd(PO_3)_3$ was prepared from Nd_2O_3 and $(NH_4)_2HPO_4$ *via* solid-phase reaction. A mixture of 1 mole Nd_2O_3 and 6 moles $(NH_4)_2HPO_4$ was thoroughly ground in an agate mortar to attain homogeneity. Then the samples were presynthesized by sintering in the following three stages: I stage: 450°C for 28 h to expel NH_3 and H_2O; II stage: 900°C for 26 h; III stage: 1050°C for 26 h. After each stage the product was thoroughly powdered and ground. The thermoanalytical investigation (by the DTA, TG, DTG methods) were performed by using a derivatograph type 3427 (MOM, Hungary) up to 1350°C (scanning rate 5 $K\cdot min^{-1}$) under air, platinum crucibles, with Al_2O_3 p.a. as the standard substance; weight of samples was 0.2 to 0.9 g. Also, a calorimeter type SETSYS^{TM} (TG-DSC; SETARAM) was used up to 1500°C (scanning rate 10 $K\cdot min^{-1}$) under argon, platinum crucibles; weight of samples was 0.001 to 0.018 g. The melting points of samples of the section in question were determined by the visual evaluation; it was not possible to determine these based on DTA heating curves. The samples for visual evaluation were prepared as follows: parent metaphosphates were weighed into fixed amounts, carefully mixed and ground in an agate mortar, then pressed into pellets and presynthesized by sintering with intermediate re-mixings. The visual evaluation consisted in taking notes of the temperature at which the sample became transparent. The visual observations were carried out using a resistance furnace (an in-house design) with Pt30Rh winding. Phase purity of the reagents was determined and the phases in the binary section were identified by powder X-ray diffraction at room temperature. Diffractometer types of Siemens D 5000 and B-TUR M 62 with CuK_α radiation were used.

RESULTS AND DISCUSSION

The $Nd(PO_3)_3$–$NaPO_3$ quasi-binary section in the Nd_2O_3–Na_2O–P_2O_5 system was investigated and the phase diagram has been proposed for the whole range of composition and temperature. Experimental work was started by checking whether an intermediate compound $NaNd(PO_3)_4$ exists in the quasi-binary section of interest. As was mentioned, the empirical formula of this binary metaphosphate indicates a molar ratio of 1:1 for $Nd(PO_3)_3$ and $NaPO_3$. Accordingly, an equimolar mixture of the above metaphosphates was heated at different temperatures (in the solid state) for different times. The phase composition of the sinters obtained was observed each time by X-ray diffraction. In such a way it was found that $NaNd(PO_3)_4$ can be obtained by the solid-state reaction *via* heating the mixture of 1 mole $Nd(PO_3)_3$ and 1 mole $NaPO_3$ between 600–650°C (12 hours). This confirmed our starting supposition, that $NaNd(PO_3)_4$ occurs as an intermediate compound in the section $Nd(PO_3)_3$–$NaPO_3$.

Based on the results of the thermoanalytical investigation (DTA, TG, DTG), it has been established that $NaNd(PO_3)_4$ melts incongruently at about 866°C to give $Nd(PO_3)_3$ and $NaPO_3$-rich liquid. DTA-heating curve reveals only one endothermic effect (at 866°C), which indicates that the compound occurs in the form of a single polymorphic modification. TG-heating curve, in turn, shows two regions: (i) plateau (from room temperature up to about 1080°C) and (ii) a region of slow, gradual (laminar) loss of mass above that temperature. The mass defect observed upon heating the phosphate $NaNd(PO_3)_4$ required explanation for an obvious reason. Initial thermoanalytical tests with the synthesized samples of heteromolar mixtures of $Nd(PO_3)_3$ and $NaPO_3$ metaphosphates, yielded TG-heating curves, including regions that could suggest a high-temperature mass loss to occur. In the $Nd(PO_3)_3$-rich part of the section in question, the onset of the change in mass was noted at about 1080°C. The onset temperature for the mass loss was composition dependent; it rose gradually with enriching the samples with $NaPO_3$. Its maximum reached about 1200°C for $NaPO_3$-rich samples. The phenomenon can be interpreted as follows: in an early investigation [5] we have found that $NaPO_3$ metaphosphate starts to decompose at 1200°C (in the liquid phase), which is accompanied by a rather big loss of mass, evident from TG curve. Thermogravimetric analysis of $Nd(PO_3)_3$, in turn, shows that a slow, small mass loss starts to appear (in the solid phase) at about 1080°C. It has been established that it is not due to decomposition of $Nd(PO_3)_3$ phosphate, or escape of P_2O_5. The mass loss visible in the TG-heating curve of presynthesized samples of the $Nd(PO_3)_3$–$NaPO_3$ section is due to the high-temperature instability of the parent metaphosphates, which does not affect the state of equilibrium of the section in question under experimental conditions employed.

The last stage of the work was the constructing of the phase diagram of the $Nd(PO_3)_3$–$NaPO_3$ section. In order to verify the results, the thermoanalytical and X-ray analysis was performed with different parent substances. Accordingly, three series of samples were investigated, namely: (i) heteromolar mixtures of $Nd(PO_3)_3$ and $NaPO_3$ metaphosphates; (ii) heteromolar mixtures of $Nd(PO_3)_3$ and $NaNd(PO_3)_4$ metaphosphates, for determination of the phase dependences in the composition range 0–50 mol % $NaPO_3$; (iii) heteromolar mixtures of $NaNd(PO_3)_4$ and $NaPO_3$ metaphosphates, for determination of the phase dependences in the composition range 50–100 mol % $NaPO_3$.

The above mixtures were presynthesized by the solid-state reaction *via* heating: (i) at 550°C for 12 h of $NaPO_3$-rich samples (those having more than 55 mol % $NaPO_3$); (ii) at 750°C for 12 h of $Nd(PO_3)_3$-rich samples (those having less than 55 mol % $NaPO_3$). The sinters obtained were powdered and thoroughly mixed for homogenizing, and then thermoanalysed. Phase composition of of those sinters was identified by X-ray powder analysis.

Depending on the initial composition of the sample, DTA curve revealed one or two thermal effects. In the composition range 0–85 mol % $NaPO_3$, the DTA-heating curves contained an endothermic peak corresponding to about 866°C. It was connected with a peritectic reaction proceeding according to the network:

$$NaNd(PO_3)_4 \xrightarrow{866\,^{\circ}\mathrm{C}} Nd(PO_3)_3 + \text{liquid}.$$

For all samples of the composition range 55–98 mol % $NaPO_3$, the DTA curves showed a large endothermic peak, corresponding to 618°C and connected with an eutectic phase transformation.

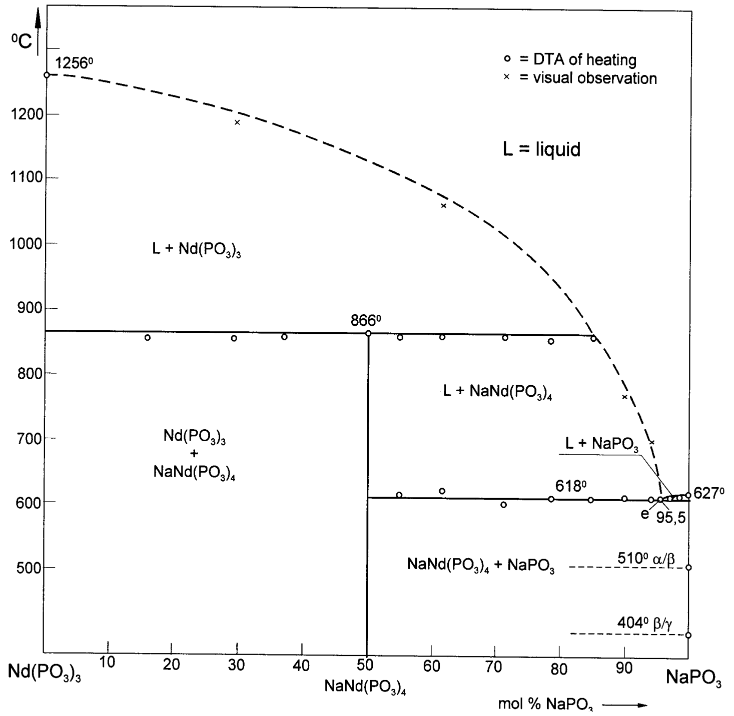

Figure 1. Phase relations in the $Nd(PO_3)_3$–$NaPO_3$ system.

In the whole composition range of the section in question, the DTA-heating curves showed no effects connected with melting of the samples or such ones were scarcely noticeable and diffuse, which makes difficulties in interpretation. Therefore, visual observation was carried out. This method enables a subjective evaluation of the melting point of a sample. For this reason the shape of liquidus curve is approximate. Pure $NaPO_3$ metaphosphate appears in its three polymorphic modifications. However, in the system of interest, any thermal effects connected with phase transitions were not revealed on the DTA-heating curves. Fig. 1 shows the phase diagram of the $Nd(PO_3)_3$–$NaPO_3$ section, constructed on the results discussed. Accordingly, the proposed liquidus curve is drawn by a dashed line.

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