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PHASE EQUILIBRIA IN THE SYSTEM $CePO_4$ - $NaPO_3$

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The system $CePO_4$ – $NaPO_3$ was investigated by differential thermal and X-ray analyses and infrared spectroscopy and its phase diagram was established. The system contains only one intermediate compound, $NaCeP_2O_7$, which melts incongruently at 800°. It exhibits a polymorphic transition at 595°. The low-temperature modification has an orthorhombic unit cell with the parameters.a = 5.28, b = 12.65, c = 4.31 Å, $\alpha = \beta = \gamma = 90°$ and V = 288.1 Å^3.

Studies on cerium(III) and sodium-cerium(III) phosphates have been conducted in our laboratory for several years. The phase equilibria in the ternary system Ce_2O_3 – Na_2O – P_2O_5 have been examined in the part rich in P_2O_5 [1, 2] and the phase diagram of the system $CePO_4$ – Na_3PO_4 has been determined [3]. The present paper describes the results of phase investigations of the previously unexamined binary system $CePO_4$ – $NaPO_3$.

According to literature data, there are pyrophosphates with the formula $M^IM^{III}P_2O_7$ (where M^I = Na, K, Rb,...; M^{III} = Al, Cr,...Y and some lanthanides). Gabelica-Robert and Tarte [4] state that these compounds may be distributed into three structural families. Anisimova *et al.* [5] report that sodium–lanthanide pyrophosphates, $NaLnP_2O_7$, crystallize in two crystallographic systems: (1) a monoclinic system (for Ln = Pr ... Gd, Dy ... Lu) and (2) and orthorhombic system (for Ln = La, Ce, Tb). To confirm this, X-ray examinations with monocrystals should be performed.

According to their composition, pyrophosphates $M^IM^{III}P_2O_7$ could occur in the system $M^{III}PO_4$ – M^IPO_3.

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Experimental

The following parent compounds of analytical reagent grade were used: $Ce(NO_3)_3 \cdot 6H_2O$, $NH_4H_2PO_4$ and $NaH_2PO_4 \cdot H_2O$. Samples in the system $CePO_4$ – $NaPO_3$ were prepared from the initial phosphates. Sodium metaphosphate, $NaPO_3$ was obtained by complete dehydration of $NaH_2PO_4 \cdot H_2O$ at 300° for 0.5 h and then at 500° for 2 h. Cerium(III) orthophosphate, $CePO_4$, was prepared from $Ce(NO_3)_3 \cdot 6H_2O$ and $NH_4H_2PO_4$ by the method provided in [6].

The methods of differential thermal and X-ray analyses and infrared spectroscopy were used in the investigations. Test samples were presynthesized by reaction in the solid phase. Thermal analysis on heating was performed with a derivatograph – C (MOM, Hungary), within the temperature range 20–1200°, in open crucibles, in an air atmosphere. The high-temperature thermal studies were performed in a resistance furnace (constructed in our laboratory) with molybdenum winding, under argon. Temperatures were read by means of an optical pyrometer, which was calibrated against the melting points of $Ca_2P_2O_7$ and Na_3PO_4.

Powder X-ray analysis at room temperature was carried out in an HZG–4 diffractometer (in the Guinier camera) with Cu – $K\bar{\alpha}$ radiation. Infrared spectra were recorded with a Specord IR–75 spectrophotometer. The samples for study were prepared in the form of KBr pellets.

Results and discussion

Preliminary thermal and X-ray investigations of the system $CePO_4$ – $NaPO_3$ confirmed the existence of the compound $NaCeP_2O_7$. The determination of the phase diagram of this system was therefore initiated with an examination of the thermal stability of $NaCeP_2O_7$. This compound can be obtained by a reaction in the solid phase: sintering of an equimolar mixtures of $CePO_4$ and $NaPO_3$ at 700° for 24 h. Figure 1 shows the IR spectrum of $NaCeP_2O_7$ (within the range 400–1200 cm^{-1}).

During thermal analysis on heating of the sample with the composition $NaCeP_2O_7$, three strong thermal effects can be noted at 595, 800 and 1260° in the DTA curves (Fig. 2). The third effect results in a mass decrement, which begins at approximately 1260° and increases regularly with temperature rise (TG curve). Hence, $NaCeP_2O_7$ is unstable at high temperatures and decomposes slowly from 1260°. To examine this process, isothermal measurement of the mass decrement was performed at 1200°. After 85 h, the

mass decrement was found to be approximately 20%. The phases which result from sintering were identified by means of X-ray analysis. It was discovered that after 2 h of sintering at 1200°, $NaCeP_2O_7$ decomposes partially to cerium(III) orthophosphate, $CePO_4$. The thermal decomposition of $NaCeP_2O_7$ in air takes place above 1200° according to the following reactions:

$$NaCeP_2O_{7(cr)} \rightarrow CePO_{4(cr)} + NaPO_{3(am)}$$

(*cr* = crystal form, *am* = amorphous). The gradual mass decrement results from the vaporization of sodium metaphosphate, $NaPO_3$. This was concluded after thermogravimetric examinations of $NaPO_3$. The results of these

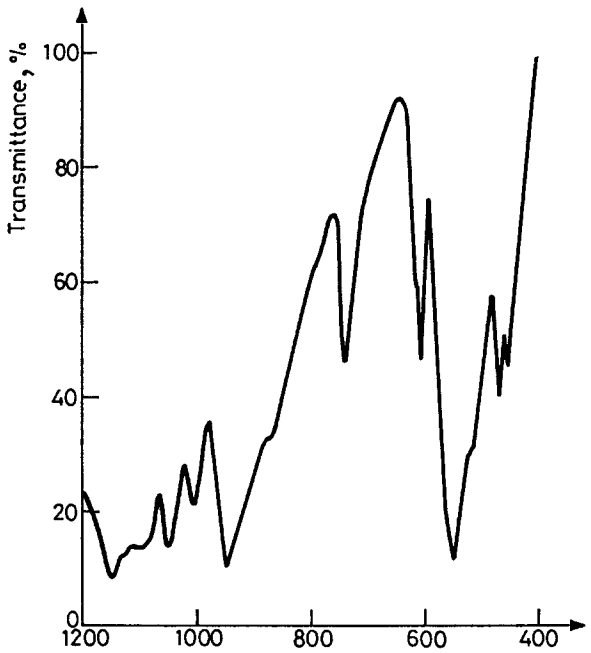

Fig. 1 IR spectra of $NaCeP_2O_7$

investigations are presented in Fig. 3. The DTA curve exhibits thermal effects at 404° and 510° (polymorphic transitions) and at 627° (melting). Further heating of liquid $NaPO_3$ causes the beginning of a mass decrement at approximately 1200°. The TG curve presents this as a downward bend.

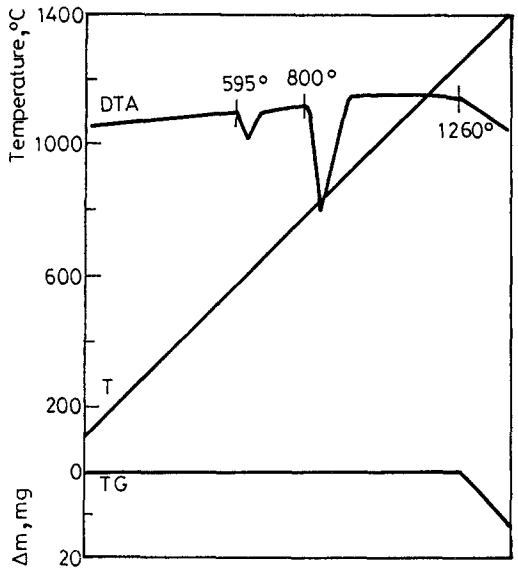

Fig. 2 T, DTA and DTG curves of $NaCeP_2O_7$, m = 510 mg, in air atmosphere

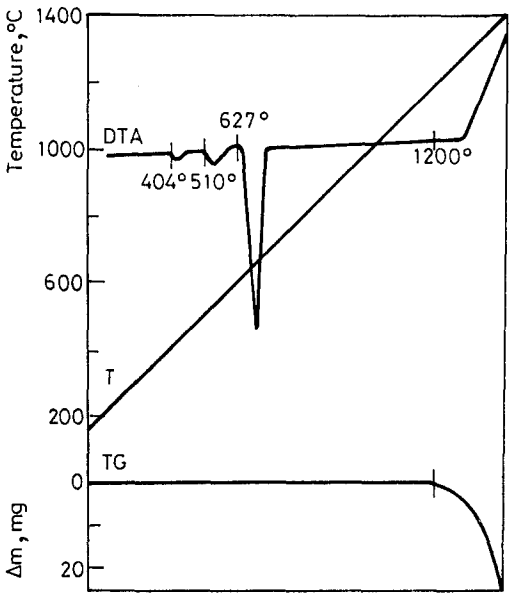

Fig. 3 T, DTA and DTG curves of $NaPO_3$, m = 330 mg, in air atmosphere

Figure 4 shows the phase diagram of the system $CePO_4$–- $NaPO_3$. The liquidus curve within the composition range 70-100 wt% of $NaPO_3$, the

solidus curve and the phase equilibria in the solid phase were determined on the basis of thermal analysis on heating. The liquidus curve within the composition range 30–70 wt% of $NaPO_3$ was determined by measuring the melting point with an optical pyrometer. Its direction is therefore approximate.

It was discovered that there is only one intermediate compound in the system. This is formed at a 1:1 molar ration of the initial phosphates (30.25 wt% of $NaPO_3$, 69.75 wt% of $CePO_4$), i.e. $NaCeP_2O_7$. This pyrophosphate melts incongruently at 800°. Thermal investigations and powder X-ray diffraction proved that $NaCeP_2O_7$ occurs in two polymorphic modifications.

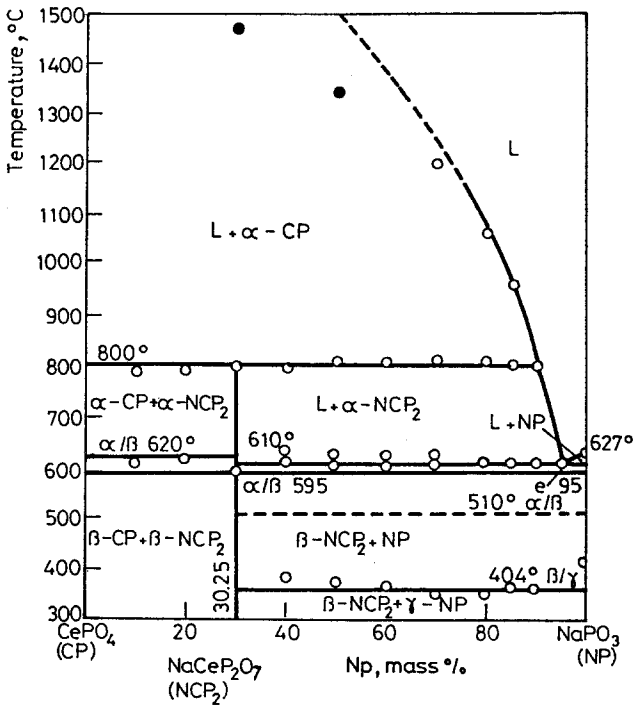

Fig. 4 Phase diagram of the system $CePO_4$ – $NaPO_3$ o–Thermal analysis (heating), •– optical

The temperature of transition (α/β) is 595° and yields a clear thermal effect in the DTA curves in nearly the whole system $CePO_4$ – $NaPO_3$. However, within the composition range 30–70 wt% of $NaPO_3$, the effect resulting from this transition occurs at somewhat higher temperatures (approx. 620–630°). It was found that the high-temperature modification, α–$NaCeP_2O_7$, can not be stabilized at room temperature by quenching in air or ice.

On the basis of X-ray powder analysis, the proposed unit cell for β–$NaCeP_2O_7$ (low-temperature modification) is orthorhombic with the following parameters: $a = 5.28$, $b = 12.65$, $c = 4.31$ Å, $\alpha = \beta = \gamma = 90°$ and $V = 288.1$ Å^3. The measurements were made with a Guinier camera, using α–corundum as internal standard. The positions of the lines were made more accurate with the method of least squares, using the LSUCR program. Indexing procedures were performed with the use of Visser's algorithm (VISIND'80 program) [7]. Intensities were estimated visually, using the graded scale of reference X-ray photographs. Table 1 presents the X-ray powder diffraction data for β–$NaCeP_2O_7$.

Table 1 X-ray data for low-temperature β–$NaCeP_2O_7$

hkl	$d_{obs.}$, Å	$d_{calc.}$, Å	Intensities
020	6.310	6.320	74
110	4.870	4.870	44
001	4.300	4.310	40
011	4.076	4.079	40
101	3.339	3.340	12
130	3.297	3.296	100
111	3.230	3.229	100
040	3.165	3.163	20
031	3.010	3.014	5
121	2.952	2.953	8
200	2.643	2.642	25
131	2.621	2.618	8
041	2.549	2.550	30
220	2.436	2.438	2
201	2.253	2.253	5
211	2.218	2.218	5
012	2.124	2.124	30
221		2.122	

Note. Orthorhombic system: $a = 5.28$, $b = 12.65$, $c = 4.31$ Å, $\alpha = \beta = \gamma = 90°$, $V = 288.1$ Å^3

In accordance with Fig. 4, in the system $CePO_4$ – $NaPO_3$ a eutectic occurs at 95 wt% of $NaPO_3$ at 610°. The peritectic reaction finishes at approximately 90 wt% of $NaPO_3$.

Sodium metaphosphate, $NaPO_3$ occurs in three known polymorphic modifications. The temperatures of the transitions are: α/β – 510° and β/γ – 404°. In the binary system under investigation, clear thermal effects resulting from the transition β/γ – $NaPO_3$ occur in the DTA heating curves. However, they are lowered by approximately 50 deg. No effects result from the transition α/β – $NaPO_3$. According to reference [8], cerium orthophosphate, $CePO_4$, yields a polymorphic transition at 700°. Our examinations proved that the temperature of this transition is 620°. In the system $CePO_4$ – $NaPO_3$, within the composition range 0-30 wt% of $NaPO_3$, the transitions α/β-$CePO_4$ and α/β – $NaCeP_2O_7$ yield one strong thermal effect at approximately 600° in the DTA curves.

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Zusammenfassung – Mittels DTA, Röntgendiffraktion und IR-Spektroskopie wurde das System $CePO_4$ - $NaPO_3$ untersucht und ein Phasendiagramm erstellt. Das System enthält nur die Intermediärverbindung $NaCeP_2O_7$, welche bei 800°C inkongruent schmilzt und bei 595°C eine polymorphe Umwandlung zeigt. Die Niedertemperatur-Modifikation besitzt eine rhombische Elementarzelle mit den Parametern a = 5.28, b = 12.65, c = 4.31, $\alpha = \beta = \gamma = 90°$, and V = 288.1 Å^3.