Phase equilibria in the system $Na_4P_2O_7$—$Zn_2P_2O_7$

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The phase equilibrium diagram of the system $Na_4P_2O_7 - Zn_2P_2O_7$ was determined by means of hot-stage microscopy, DTA, and X-ray powder diffraction. The system is of quasi-binary character. There is one intermediate compound in it ($Na_2ZnP_2O_7$) which melts congruently at 805°C. It crystallizes in the tetragonal system with unit cell parameters $a = 7.6919(9)$ A, $c = 10.2726(8)$ A.

The system $Na_4P_2O_7 - Zn_2P_2O_7$ has been DTA studied by *Berul'* and *Voskresenskaya* [1]. The authors concluded on the presence of three intermediate compounds ($3Zn_2P_2O_7 \cdot 2Na_4P_2O_7$, $Zn_2P_2O_7 \cdot Na_4P_2O_7$, and $2Zn_2P_2O_7 \cdot 3Na_4P_2O_7$). Each of the intermediate compounds was reported to melt congruently. The results were of informative character. The compound $Zn_2P_2O_7 \cdot Na_4P_2O_7$ ($Na_2ZnP_2O_7$) was originally described by *Klement* [2]. According to *Krivovyazov, Voskresenskaya*, and *Palkina* [3] this compound melts congruently at 781°C.

Experimental

The presynthesized $Na_4P_2O_7$ and $Zn_2P_2O_7$ were used for the preparation of samples. $Na_4P_2O_7$ was prepared through recrystallization of $Na_4P_2O_7 \cdot 10H_2O$, its dehydration at 105°C, and heating at 500°C. The second compound, $Zn_2P_2O_7$, was prepared by evaporation of the water solution containing $Zn(NO_3)_2$ and $NH_4H_2PO_4$ and by heating the dry precursor at 800°C. $Zn(NO_3)_2$ was prepared by dissolution of the Zn metal (anal. grade) in HNO_3 (anal. grade).

Homogenized mixtures of $Na_4P_2O_7$ and $Zn_2P_2O_7$ were heated at 600°C for 10 hrs, rehomogenized and reheated for another 10 hrs.

The crystalline phases present were identified by X-ray powder diffraction using a Philips 1540 diffractometer and CuK_α radiation. Diffraction pattern of $Na_2ZnP_2O_7$ was taken at a scanning rate $1/8°$ 2Θ/min with silicon ($a_0 = 5.43062$ A) as an internal standard. Unit cell parameters were least-squares refined using the program of *Lindqvist* and *Wengelin* [4].

Single crystals of $Na_2ZnP_2O_7$ were prepared by cooling the melt containing 50 mole % $Na_4P_2O_7$. Unit cell parameters were measured from precession and Weissenberg photographs. The density was measured by flotation.

Liquidus temperatures were determined using a Griffin hot-stage microscope. The temperature was measured by $Pt - 5\%$ Rh/$Pt - 20\%$ Rh thermocouple calibrated against transition of K_2SO_4 (583°C) and melting points of NaCl (800°C) and K_2SO_4 (1069°C).

The thermocouple of the microscope serves as a heating element and the sample holder [5, 6]. About 0.5 mg of the sample is taken into analysis.

The reproducibility of the temperature measurement was within $\pm 2°C$.

DTA records were taken on a Derivatograph apparatus (MOM, Budapest) at a heating rate 10°C/min and the sample weight of 350 mg. The measurements were conducted at the half sensitivity of the instrument. The temperature scale was checked against the melting point of NaCl.

Results and discussion

Phase diagram of the system $Na_4P_2O_7 - Zn_2P_2O_7$

The phase diagram of the system $Na_4P_2O_7 - Zn_2P_2O_7$ is presented in Fig. 1. The full circles denote the liquidus temperatures as measured by the hot-stage microscope. The open circles correspond to endothermic signals on DTA curves. The temperatures of isothermal reactions in the system were derived from the starts of the deflections of DTA peaks. Liquidus temperatures were derived from the points of intersections of base lines with the tangents to descending parts of the DTA signals. Graphical records allowed us to determine the temperature with a precision $\pm 2°C$. The read off temperature was rounded up on the nearest value divisible by 5.

The system $Na_4P_2O_7 - Zn_2P_2O_7$ is of binary character. One intermediate compound $Na_2ZnP_2O_7$ is present in the system undergoing no transition and melting congruently at 805°C. The following parameters of eutectic points are obtained: $e_1 = 24$ wt % $Na_4P_2O_7$, 645°C and $e_2 = 65$ wt % $Na_4P_2O_7$, 705°C. The melting temperature of $Na_2ZnP_2O_7$ (805°C)
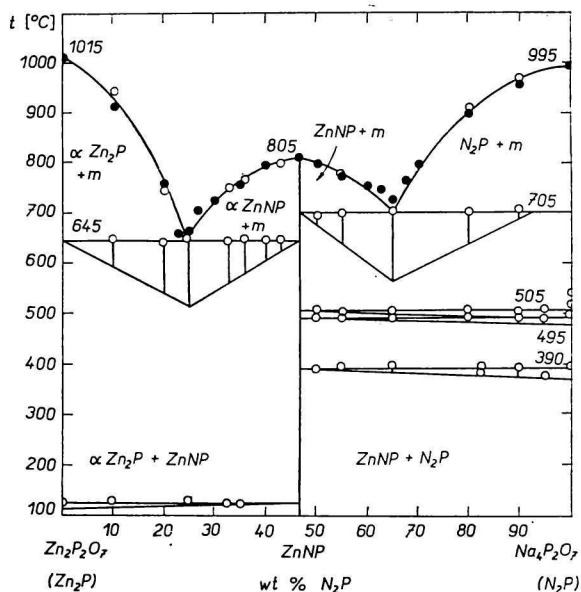
Fig. 1. The phase diagram of the system $Zn_2P_2O_7 - Na_4P_2O_7$.
● hot-stage microscope; ○ DTA.

can be compared only with the value 781°C determined by *Krivovyazov et al.* [3] during the study of the other section ($NaPO_3-ZnO$) of the system $Na_2O-ZnO-P_2O_5$. The difference can be accounted for by different starting materials. Our result is favoured by the higher value of the melting temperature.

Melting point of $Zn_2P_2O_7$ (1015°C) is in good agreement with the value of 1017°C determined by *Katnack* and *Hummel* [7]. Melting temperature of $Na_4P_2O_7$ agrees well with the recent literature data [8] (998°C) and [9] (995°C).

For $Na_4P_2O_7$ the four transitions are given in [8, 9] and six transitions in [10]. In the case of the samples lying in the two-phase region we observed the transitions at temperatures 390, 495, and 505°C. The sample of the pure $Na_4P_2O_7$ exhibited signals at 390, 505, 520, and 540°C. The temperatures of the last two signals could not be read off from the starts of deflections because of the superposition of peaks.

Crystallographic data for $Na_2ZnP_2O_7$

The precession and the Weissenberg photographs exhibited a system of strong reflections, corresponding to the tetragonal unit cell ($a_0 = 7.6919$ A, $c_0 = 10.2726$ A), and in addition, a system of extremely weak reflections. Their occurrence could have been described by unit cell parameters $4a_0$, c_0. These reflections appeared on the overexposed film patterns only; in the powder pattern they had not been discernible. The powder pattern of $Na_2ZnP_2O_7$ was indexed therefore on the basis of the unit cell with parameters a_0, c_0 (Tables 1 and 2). The crystal structure analysis of the compound is in progress.

Table 1

The crystallographic data for $Na_2ZnP_2O_7$

Tetragonal symmetry	
a	= 7.6919(9) A
c	= 10.2726(8) A
V	= 607.8 A³
Z	= 4
ϱ_c	= 3.11 g cm⁻³
ϱ_m	= 3.12(2) g cm⁻³

The compound $Na_2ZnP_2O_7$, for which the powder diffraction pattern was measured (Table 2), was prepared by heating the sample containing 60 wt % $Na_4P_2O_7$ above the eutectic temperature (705°C), its slowly cooling, and consequent dissolution of the excessive $Na_4P_2O_7$ in water. The sample prepared in the above-specified way exhibited, in comparison to the sample prepared by the reaction in the solid state, the texture manifested by the fact that the intensity of the 103 diffraction attained the higher value than the diffraction 202 (Table 2). The effect was eliminated through the filling of the sample holder from the side [11].

The indexing of the powder pattern and the refinement of unit cell parameters was done on the basis of 15 diffraction lines with well defined intensity profiles. The rest of lines, the weak intensity lines in particular, were indexed by comparing the observed and calculated values. Internal standard allowed us to determine the position of lines

Table 2

Powder diffraction data for $Na_2ZnP_2O_7$

d_{obs}	d_{calc}	hkl	I/I_0
6.153	6.157	101	2
5.452	5.439	110	1
5.136	5.136	002	100
3.846	3.846	200	5
3.738	3.734	112	20
3.4402	3.4400	210	20
3.1287	3.1282	103	17
3.0805	3.0786	202	40
2.898	2.897	113	15
2.859	2.858	212	45
2.720	2.719	220	10
2.568	2.568	004	1
2.4329	2.4324	310	25
2.4041	2.4034	222	3
2.3223	2.3223	114	8
2.1983	2.1983	312	15
2.1357	2.1357	204	2
2.0579	2.0579	214	3
1.9853	1.9849	105	1
1.9224	1.9230	400	1
	1.9220	115	
1.8676	1.8672	224	10
1.7663	1.7660	314	17
1.7204	1.7200	420	5
1.7121	1.7121	006	2
1.6309	1.6309	422	12
1.5640	1.5641	206	2

with a precision of $\pm 0.01°$ 2Θ. Inside this angular value the systematic correction for the line positions was applied which led to the lowering of the standard deviations of the unit cell parameters. The intensities were derived from the peak heights.

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