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Phase Coexistence in the System $Na_2O—P_2O_5—ZrO_2$

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On the basis of the X-ray diffraction the phase compatibility of the system $Na_2O—P_2O_5—ZrO_2$ was determined at subsolidus temperatures (350—1200 °C). There are nine binary and three ternary phases present in the system. The phase compatibility diagram is presented.

The contribution presents basic study of the phase coexistence at subsolidus temperatures. The study relies on a knowledge of the phase coexistence in the binary subsystems: $Na_2O—P_2O_5$ [1, 2], $Na_2O—ZrO_2$ [3], and $P_2O_5—ZrO_2$ [4, 5], respectively. It is also based on the existence of ternary phases, which are present in the quasi-binary system $N_3P—Z_3P_2$* [6]. There are three compounds (NZ_4P_3, NZP, $N_5Z_2P_3$) in this phase diagram. The first of them is the end member of the solid solution at which the quaternary "Nasicon" ($Na_3Zr_2Si_2PO_{12}$) is constituted. The figurative points of solid solutions $Na_{5-4x}Zr_{1+x}P_3O_{12}$ ($N_5Z_2P_3$) ($0.04 < x < 0.11$) and of the phase ε [$Na_7Zr_{0.5}(PO_4)_3$] (N_7ZP_3) are located in this section, too.

EXPERIMENTAL

Following two ways of preparation of samples were used:

a) By the solid state reaction in which the homogenized mixtures of individual compounds in an agate mortar were used as starting powders. Following compounds were taken for preparation of powder mixtures: ZrO_2, Na_2CO_3, $NH_4H_2PO_4$, $NaH_2PO_4 \cdot 2H_2O$.

b) By the sol/gel procedure in which the precursor gel was obtained from a mixed and tempered solution. The solution with the desired ratio w_r of Na_2O, P_2O_5, and ZrO_2 was prepared volumetrically using 0.169 M-zirconium acetate, 0.353 M-$NaNO_3$, and 0.261 M-$NH_4H_2PO_4$.

All the chemicals used were of anal. grade.

Prepared powder mixtures were heated in the platinum crucible in an electric resistance furnace. The attainment of the phase equilibrium was checked by X-ray phase analysis. X-ray patterns were taken on the DRON-0.5, Cu*Kα* radiation. The interpretation of X-ray diffraction patterns was performed using the published data mainly [4, 5, 7—9].

RESULTS AND DISCUSSION

The results of the phase analysis of samples are presented in Table 1. In this table also the mole fractions of components and the heating schedules of samples are given.

The phase compatibility diagram was constructed using the obtained data (Fig. 1).

Only those ternary phases are present in the system, the figurative points of which lie on the tie line $N_3P—Z_3P_2$. All these compounds (as their structural formulae show) belong to orthophosphates.

On the orthophosphate join there exists also the phase ε the stoichiometry of which is close to

*The chemical composition of individual compounds is expressed in a notation at which: N = Na_2O, Z = ZrO_2, S = SiO_2, P = P_2O_5. Then for example: $NZ_4P_3 = Na_2O \cdot 4ZrO_2 \cdot 3P_2O_5 = Na_2Zr_4P_6O_{24} = 2NaZr_2P_3O_{12}$.

Table 1. Compositions of Starting Mixtures, Their Heating Schedules, and Results of Phase Analysis

Sample	$x(Na_2O)$ / %	$x(P_2O_5)$ / %	$x(ZrO_2)$ / %	θ/°C	t/h	Phase analysis results
1	25	50	25	500	200	NP, ZP
2	29.5	42.5	28	500	200	NP, NZ_4P_3
3	44	46	10	600	200	NP, N_5P_3, NZ_4P_3
4	40	40	20	600	200	NP, N_5P_3, NZ_4P_3
5	50	38	12	500	200	N_5P_3, NZ_4P_3
6	35	35	30	600	200	N_2P, NZ_4P_3
7	55.5	34.5	10	600	200	N_2P, NZ_4P_3
8	50	17	33	800	200	γ-N_3P, Z
9	65	15	20	800; 1000	150; 1	α-N_3P, NZ
10	6	44	50	600; 1000; 1200	40; 90; 10	NZ_4P_3, ZP
11	42.9	14.2	42.9	930	25	Z, α-N_3P
12	31.3	18.7	50	900	20	Z, N_5P_3
13	25	25	50	900	20	Z, NZP
14	6.7	26.7	66.6	950	20	NZ_4P_3, α-Z_2P
15	5.6	38.8	55.6	880	25	NZ_4P_3
16	7.1	42.9	50	950	20	NZ_4P_3, ZP
17a	20	60	20	480	35	ZP, NP
17b	20	60	20	350	35	ZP, NP
18	28.6	42.8	28.6	550	20	NZ_4P_3, NP, (ZP)
19	60	10	30	950	20	NZ, N_3P, (Z)
20	50	33.3	16.7	600	30	N_2P, N_5P_3
21	53.8	30.8	15.4	600	30	N_2P, NZP

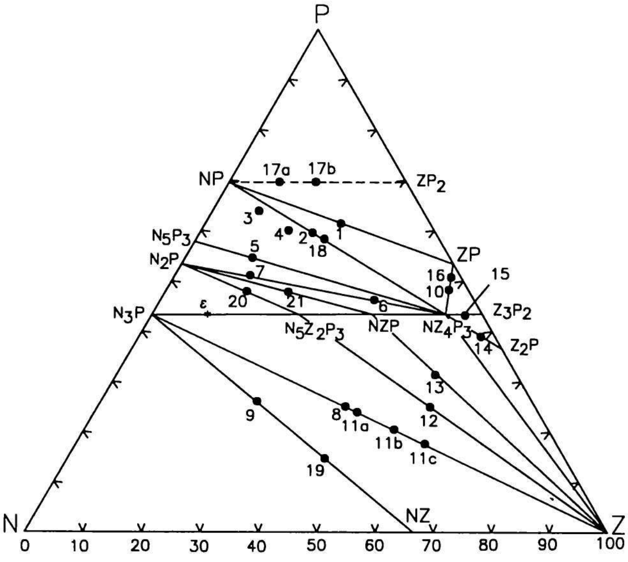

Fig. 1. Phase compatibility diagram of the system $Na_2O—P_2O_5—ZrO_2$.

$Na_7Zr_{0.5}(PO_4)_3$. This phase is stable only above the temperature 980 °C [6]. Its coexistence with N_2P or Z was not experimentally verified.

The sample No. *15* represents the single rhombohedral phase — a solid solution , with the end members NZ_4P_3 and Z_3P_2, respectively [4]. The positions of diffractions are close to those found in the calculated diffraction patterns of NZ_4P_3 [9].

The join of two corresponding pyrophosphates ($N_2P—ZP$) does not represent the quasi-binary system.

The polyphosphate ZP_2 is up to now the only compound from the system $Na_2O—P_2O_5—ZrO_2$ with the content of P_2O_5 higher than 50 mole %. If it is supposed that in the area NP—ZP—P of the studied system no further phase is present, then ZP_2 should coexist with NP. Experimental verification of phase compatibilities in this area of the system is restricted by the low temperature of the melt creation and by the volatility of P_2O_5 at higher temperatures.

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