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The Phase Equilibria Study in the System $Na_4P_2O_7$-$Mg_2P_2O_7$

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The phase equilibria in the system $Na_4P_2O_7$–$Mg_2P_2O_7$ were studied by means of DTA, hot stage microscopy and X-ray diffraction analysis. There is one intermediate compound in the system which melts congruently at 832°C of chemical composition $Na_7Mg_{4.5}(P_2O_7)_4$. It crystallizes in the triclinic system with unit cell constants: $a = 10.882(1)$, $b = 9.734(1)$, $c = 6.372(1)$ Å; $\alpha = 112.49(1)$, $\beta = 99.63(1)$, $\gamma = 107.40(1)°$.

Introduction

The phase equilibria in the system $Na_4P_2O_7$–$Mg_2P_2O_7$ were studied by Berul and Voskresenskaya (*1*). They confined their study up to the concentration 55 mole % $Mg_2P_2O_7$. According to them, two compounds exist ($3Na_4P_2O_7 \cdot 2Mg_2P_2O_7$, $Na_4P_2O_7 \cdot Mg_2P_2O_7$) and both melt congruently. The compound $Na_4P_2O_7 \cdot Mg_2P_2O_7$ ($Na_2MgP_2O_7$) was originally described by Klement (*2*).

Experimental

The samples were prepared by slow evaporation of diluted water solutions of $Mg(NO_3)_2$, $NaNO_3$ and $NH_4H_2PO_4$. The following reagents were used: Mg-metal (99.9%), $NaNO_3$ (analytical-reagent grade, recrystallized from the melt), and $NH_4H_2PO_4$ (analytical-reagent grade, dried at 105°C).

During evaporation of solutions, no preferential precipitation occurred. After evaporation, the dry precursors were heated at 700°C for 20 hours.

Phases present at subsolidus temperatures were identified by X-ray powder diffraction analysis. Powder patterns were taken on a Philips 1540 diffractometer using filtered Cu$K\alpha$ radiation. The powder pattern of $Na_7Mg_{4.5}(P_2O_7)_4$ (Table I) was taken at a scanning rate 1/2° 2θ/min., using silicon as an internal standard. Unit cell constants of this compound were determined from precession photographs (*3*). These constants were used for indexing the powder pattern (Table I) and for least squares refinement of final lattice constants (Table II) (*4*). The end members of the system, $Na_4P_2O_7$ and $Mg_2P_2O_7$, were identified by their powder patterns (*5*, *6*).

DTA measurements were performed on an apparatus of our own construction (heating rate 5–8°C/min.). The sample was placed in a Pt–crucible in amount of 250 mg. Temperature was measured by a Pt vs Pt-10%Rh thermocouple, which was calibrated against melting points of $NaNO_3$, NaCl and K_2SO_4.

Liquidus temperatures were measured in air using a Griffin–Telin hot stage microscope equipped with a Pt-5%Rh vs Pt-20%Rh thermocouple. The thermocouple serves simultaneously as heating element and sample-holder (*7*). Cca 0.5 mg amount of sample is taken for analysis. The reproducibility of temperature measurements (±3°C) indicated the homogeneity of sample. The thermocouple was calibrated against the transition point of K_2SO_4 (573°C) and melting points of NaCl and K_2SO_4.

Single crystals of $Na_7Mg_{4.5}(P_2O_7)_4$ were prepared by slowly cooling a melt containing 50 mole % $Mg_2P_2O_7$. Density was measured by immersion (*8*).

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TABLE I

POWDER DIFFRACTION DATA FOR $Na_7Mg_{4.5}(P_2O_7)_4$

$hk1$	d_{obs}	d_{calc}	I_{obs}
1 0 0	9.840	9.840	vvw
0 −1 0	8.246	8.248	vvs
1 −1 0	8.110	8.110	vw
1 0 −1	5.697	5.696	vw
0 0 −1	5.583	5.578	vvw
1 1 0	5.362	5.357	vw
1 1 −1	5.320	5.318	vw
2 −1 0	5.236	5.243	m
1 1 1	5.064	5.064	w
2 0 0	4.919	4.920	vw
1 −2 0	4.498	4.496	w
0 −1 1	4.432	4.430	vvw
1 −2 1	4.333	4.332	m
1 0 1	4.296	4.299	w
1 −1 −1	4.237	4.238	m
0 −2 0	4.122	4.124	vs
2 −2 0	4.055	4.055	vw
2 1 −1	3.935	3.937	w
2 −1 −1	3.914	3.916	w
0 −1 −1	3.867	3.869	s
1 2 −1	3.797	3.799	vs
2 −1 1	3.732	3.732	vw
2 −2 1	3.620	3.621	m
3 −1 0	3.576	3.576	m
1 2 0	3.556	3.356	w
3 0 0	3.281	3.280	vw
1 1 1	3.185	3.184	w
2 −2 −1	3.019	3.020	m
1 −2 −1	3.0155	3.0159	w
2 −3 1	3.0135	3.0135	w
1 −3 0	2.9742	2.9729	s
2 1 −2	2.9155	2.9154	vw
1 −2 2	2.8707	2.8703	vs
0 −2 −1	2.7632	2.7639	vs
0 −3 0	2.7486	2.7494	vs
3 −3 0	2.7036	2.7032	m
3 1 0	2.7002	2.7005	m
3 2 0	2.6790	2.6784	w
4 −1 0	2.6687	2.6662	m
4 −2 0	2.6213	2.6218	s
3 0 −2	2.5687	2.5679	m
2 −2 2	2.6213	2.6218	vw
4 0 0	2.4597	2.4599	vw
3 2 −1	2.4404	2.4403	w
2 −3 2	2.4264	2.4256	vw
1 3 0	2.4106	2.4106	vw
3 −1 −2	2.3775	2.3779	m
4 1 −1	2.3258	2.3260	vvw
3 2 −2	2.2974	2.2976	w
1 −3 −1	2.2729	2.2727	vw
4 −1 1	2.2397	2.2396	w
3 2 0	2.1782	2.1786	m
4 −1 −2	2.1514	2.1514	s
4 1 0	2.1358	2.1357	s
5 −1 0	2.1136	2.1138	w

TABLE II

CRYSTALLOGRAPHIC DATA FOR $Na_7Mg_{4.5}P_8O_{28}$

Triclinic, space group $P\bar{1}$

$a = 10.882(1)$ Å $\alpha = 112.49(1)$ Å
$b = 9.734(1)$ $\beta = 99.63(1)$
$c = 6.372(1)$ $\gamma = 107.40(1)$
$V = 563.9$ Å^3
$Z = 1$
$\rho_m = 2.83$ g cm^{-3}
$\rho_c = 2.84$ g cm^{-3}

Results and Discussion

Our results of the phase equilibria study are presented in Fig. 1. The open circles represent liquidus temperatures as measured by the hot stage microscope, and triangles correspond to the temperature of thermal effects on DTA curves.

These results show that the $Na_4P_2O_7$–$Mg_2P_2O_7$ system is quasi-binary, with one intermediate compound. The existence of a second compound, as indicated by Berul and Voskresenskaya (*1*), was not confirmed.

The X-ray powder diffraction revealed only three phases. Two of them were end members of the system ($Na_4P_2O_7$, $Mg_2P_2O_7$). The indexed powder diffraction pattern of the intermediate phase is presented in Table I.

The intermediate phase does not undergo any modification and melts congruently at 832°C. Its chemical composition corresponds to the formula $Na_7Mg_{4.5}(P_2O_7)_4$.

Klement's analysis of crystals of the intermediate phase (*2*) also allowed for the assumption that this is a quasi-binary system. He found that the molar ratio ($MgO + Na_2O$)/P_2O_5 equals 2.0.

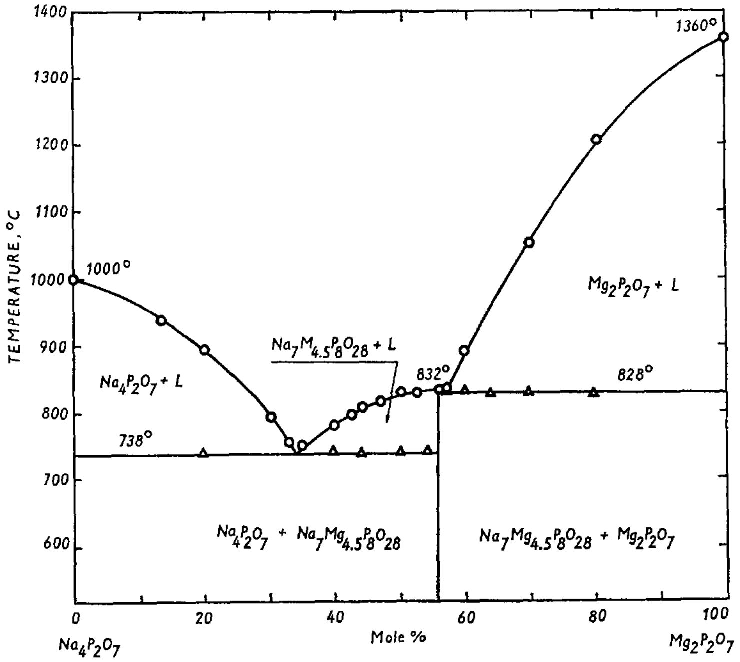

FIG. 1. The phase diagram of the system $Na_4P_2O_7$–$Mg_2P_2O_7$.

Klement further stated that the analysed compound contained 53.0 mole % of $Mg_2P_2O_7$, and therefore concluded that the formula $Na_2MgP_2O_7$ represents the analysed phase. However, as shown in Fig. 1, this formula does not adequately represent the chemical composition. On the basis of DTA and hot stage microscopy results, only one conclusion may be drawn, i.e., the intermediate phase should contain more than 54.0 mole % of $Mg_2P_2O_7$. All thermal effects accompanying the reaction at 828°C were approximately of the same size and did not allow for any conclusions as to the chemical composition.

The congruent melting of the intermediate phase followed from the results of hot stage microscopy, which revealed that isolated crystals of this phase melted at 832°C, and above this temperature no primary crystals of $Mg_2P_2O_7$ were observed. The congruent melting of the compound limits its possible concentration between 54.0 and 58.0 mole % of $Mg_2P_2O_7$ (Fig. 1).

The crystal structure of $Na_7Mg_{4.5}(P_2O_7)$ was solved by direct methods from the three-dimensional X-ray data. The intensities of 2111 independent reflections were measured photometrically using integrated equiinclination Weissenberg photographs of levels *hk*0–*hk*5. Absorption and Lorentz–polarization corrections were applied ($\mu = 93.9\ \mathrm{cm}^{-1}$ for the Cu*K*α radiation). The space group $P\bar{1}$ was established from the statistical test. The coordinates and temperature parameters of atoms, together with the scale factor were refined by the least-squares program written in the Chemical Institute of the Aarhus University by Drs. R. Hazzel, J. Nyborg, J. Danielsen and S. Lauesen for a GIER computer. The block-diagonal approximation and the weighting scheme proposed by Hughes (*9*). The reliability index $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ for the final atomic coordinates and corresponding individual anisotropic temperature parameters decreased to 7.1 %. The detailed crystal structure analysis of $Na_7Mg_{4.5}(P_2O_7)_4$ will be published in a special paper. We only briefly present here some conclusions related to the phase equilibria study in the system $Na_4P_2O_7$–$Mg_2P_2O_7$.

From the unit cell constants and the density (Table II), there seem to be only two possible formulas: $Na_2MgP_2O_7$ ($Z = 4$) and $Na_6Mg_5(P_2O_7)_4$ ($Z = 1$). In spite of the agreement with Klement's result (*2*), the first formula is not acceptable according to Fig. 1. The second formula (62.5 mole % of $Mg_2P_2O_7$) strongly implies incongruent melting, which was not observed by hot stage microscopy. Crystal structure analysis did not favor either of these formulas. The reliability factor R in both cases was 22%.

According to X-ray structure analysis, the crystal structure of $Na_7Mg_{4.5}(P_2O_7)_4$ consists of Na^+, Mg^{2+} and $P_2O_7^{4-}$ ions. The triclinic cell contains 49 electron density maxima, in which 8P, 6Na, 4Mg and 28O could be localized. The remaining three maxima are occupied by 2Na and 1Mg (at symmetry centre) with an occupation factor 0.5. Such an arrangement of atoms corresponds to the composition $Na_7Mg_{4.5}(P_2O_7)_4$, which is in a very good agreement with the phase equilibria study. A short interatomic Na–Mg distance (1.83 ± 0.01 Å) between atomic sites with occupation factor 0.5 excludes the unit cell content $Na_8Mg_5(P_2O_7)_4$. The crystal structure consists of a statistical occurrence of unit cells containing $Na_8Mg_4(P_2O_7)_4$ and $Na_6Mg_5(P_2O_7)_4$.

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