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THERMODYNAMIC STUDY OF THE SOLID–LIQUID EQUILIBRIA IN THE SYSTEMS M^IPO_3–$Pr(PO_3)_3$ (M^I=Na, Rb, Cs OR Ag)

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Abstract

A previously established equation of a stoichiometric phase liquidus curve was applied to determination of the phase diagrams of the systems M^IPO_3–$Pr(PO_3)_3$ (with M^I=Na, Rb, Cs or Ag).

The temperature, enthalpy and entropy of fusion were calculated for each solid phase with the exception of silver polyphosphate, the crystallization field of which was very limited.

The enthalpy of fusion of the polyphosphate $Pr(PO_3)_3$ was determined from the DTA curve.

The melting enthalpy of $Pr(PO_3)_3$ calculated from the different binary systems was approximately equal to the measured value. The calculated temperatures and compositions were in good agreement with those determined experimentally.

Keywords: enthalpy, diagrams, phase equilibrium, phase odymum phosphates

Introduction

Experimental study, graphical representation, the exploitation of phase diagrams and the critical evaluation of experimental values involve convenient models. The coherence of these models with thermodynamic constraints must always be checked. This prevents an erroneous representation of phase equilibria and allows a better understanding and interpretation of experiments or the calculation of significant thermodynamic data.

This paper presents an analysis, processing and thermodynamic exploitation of solid-liquid equilibria curves of the systems M^IPO_3–$Pr(PO_3)_3$ (with M^I=Na,

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Rb, Cs or Ag). In order to refine and to interpret the experimental data, we have applied to these systems a semi-empirical equation [1–3] that has already used with success for similar binary systems, and many binary water–salt systems.

A complementary study involving calorimetry was undertaken to control the thermodynamic values of monovalent metal polyphosphates [3] and praseodymium polyphosphate, determined by liquidus curve computation.

Experimental

The melting enthalpies of monovalent metal polyphosphates were determined with a Seteram DSC 111 differential calorimeter coupled to a Hewlett-Packard calculator allowing, through an appropriate program, integration of the different thermal 'effects' by the scanning method. The calorimeter correction factor was introduced into the program. Samples of 0.2 g, in a stainless steel measuring cell, were used and the furnace heating rate was 10 K $\min^{-1}$.

The melting enthalpy of praseodymium polyphosphate was determined with a Setaram Micro DTA TAG24 apparatus coupled to a Hewlett-Packard calculator allowing, through an appropriate program, integration of the different thermal 'effects' by the scanning method. The melting enthalpies of K_2SO_4 and CaF_2 [4] were utilized to calibrate the apparatus. Samples of 0.05 g, in a platinum measuring cell, were used and the furnace heating rate was 10 K $\min^{-1}$.

The phase equilibrium diagrams of the binary systems M^IPO_3–$Pr(PO_3)_3$ (with M^I=Na, Rb, Cs or Ag) were established by using differential thermal analysis (DTA), according to the method of Mazières [5], with an M5 Micro DTA Setaram and a PTC-10A Micro DTA Rigaku apparatus. The furnace heating rate was 10 K $\min^{-1}$. Samples of M^IPO_3 and $PrP_3O_9{\cdot}3H_2O$ in different concentration ratios, reduced to fine powders, were prepared in silica crucibles. The temperatures and the annealing times of the samples varied with their composition.

For the differential thermal analysis, the crucibles containing the above samples and the reference α-Al_2O_3 were made of platinum. A Pt/Pt–Rh thermocouple was used at temperatures higher than 1273 K; below this temperature, a Pt/Platinel thermocouple was sufficient.

Results

The calorimetric study of the melting enthalpies was limited by two factors: the available apparatus did not allow measurements at temperatures higher than 1100 K, and the binary intermediate compounds underwent peritectic decomposition upon heating.

The melting point of $Pr(PO_3)_3$ is higher than 1100 K, and therefore the melting enthalpy for this compound was determined via the DTA curve.

The melting enthalpies of M^IPO_3 and $Pr(PO_3)_3$ are presented in Table 1.

The DTA results for M^IPO_3–$Pr(PO_3)_3$ (M^I=Na [6], Rb [7], Cs [8] and Ag [9]) are presented in Tables 2–5. The phase equilibrium diagrams obtained are depicted in Figs 1–4.

Table 1 Melting enthalpies of $Pr(PO_3)_3$ and M^IPO_3 (M^I=Na, Rb, Cs or Ag)

Components	$T_{\mathrm{fus\ exp.}}$/K	$\Delta H_{\mathrm{fus\ exp.}}$/kJ mol^{-1}
$Pr(PO_3)_3$	1529	71.3
$NaPO_3$	917	22.2
$RbPO_3$	1068	11.1
$CsPO_3$	1004	10.1
$AgPO_3$	773	11.7

Table 2 Phase transformations in the system $NaPO_3$–$Pr(PO_3)_3$

x[a]	T_E/K[b]	T_P/K[c]	T_F/K[d]
0.0			917
2.5	901		909
5.0			901
7.5	901		973
10.0	901		1021
15.0	901		1065
20.0	903		1105
25.0	903		1131
30.0	901	1149	1190
35.0	899	1150	1243
40.0	898	1155	1285
45.0	898	1157	1305
50.0		1145	1353
55.0		1147	1353
60.0		1149	1395
65.0		1141	1411
70.0		1143	1415
75.0		1141	1433
80.0		1141	1453
90.0		1146	1509
100.0			1529

[a] x, mol% of $Pr(PO_3)_3$, [b] T_E, eutectic temperature, [c] T_p, peritectic temperature, [d] T_F, melting temperature

Table 3 Phase transformations in the system $RbPO_3$–$Pr(PO_3)_3$

x^a	T_t/K^b	T_E/K^c	T_{P1}/K^d	T_{P2}/K^d	T_F/K^e
0.0	682				1068
5.0	680	941			1039
7.5	673	946			999
10.0	678	937			980
12.5	680	941			949
15.0	680	940			988
17.5	679	941	988		1044
20.0	689	941	992		1071
25.0	683	941	997		1123
30.0	685	941	1005		1147
33.0			993		1159
40.0			981	1172	1202
45.0			980	1170	1245
50.0				1173	1293
60.0				1159	1328
70.0				1151	1385
80.0				1143	1437
90.0				1145	1483
100.0					1529

$^a x$, mol% of $Pr(PO_3)_3$, $^b T_t$, phase transformation temperature of $RbPO_3$, $^c T_E$, eutectic temperature, $^d T_{P1}$, T_{P2}, peritectic temperatures, $^e T_F$, melting temperature

Table 4 Phase transformations in the system $CsPO_3$–$Pr(PO_3)_3$

x^a	T_t/K^b	T_E/K^c	T_{P1}/K^d	T_{P2}/K^d	T_F/K^e
0.0	763				1004
2.5	784	897			991
5.0	785	903			971
7.5	778	899			942
10.0	785	896			913
12.5	769	897			909
15.0	788	901			947
17.5	770	891			993
20.0	785	889			985
22.5	763	883	1037		1051
25.0	784	886	1045		1108

Table 4 Continued

x^a	T_t/K^b	T_E/K^c	T_{P1}/K^d	T_{P2}/K^d	T_F/K^e
27.5	769		1025		1129
30.0	784	882	1041		1151
35.0			1048		1169
40.0			1045	1180	1245
45.0				1182	1297
50.0				1180	1333
55.0				1173	1359
60.0				1175	1391
70.0				1171	1443
80.0				1173	1483
90.0					1505
100.0					1529

[a] x, mol% of $Pr(PO_3)_3$, [b] T_t, phase transformation temperature of $CsPO_3$, [c] T_E, eutectic temperature, [d] T_{P1}, T_{P2}, peritectic temperatures, [e] T_F, melting temperature

The study revealed the existence of two intermediate compounds, $M^IPr(PO_3)_4$ and $M^I_2Pr(PO_3)_5$, for M^I=Rb or Cs, or only one compound, $M^IPr(PO_3)_4$, for M^I= Na or Ag.

Choice of a model for calculation of solid–liquid equilibria in the systems M^IPO_3–$Pr(PO_3)_3$

Equation of a liquidus curve

Several models have been proposed [10–12] for the description of phase diagrams.

As stated in a publication concerning the critical evaluation of binary systems [3], the models used to describe polyphosphate systems must comply with several constraints:

– the solid phases (M^IPO_3, $Pr(PO_3)_3$, $M^IPr(PO_3)_4$ and $M^I_2Pr(PO_3)_5$) are stoichiometric;

– the equation fitting the liquidus curve must never be in contradiction with thermodynamic laws; and

– the model can be extended to systems exhibiting an associated liquid phase.

The selected model presented previously [3] was re-examined [13] and applied to molten salt systems. The analytical expression perfectly describes the

Table 5 Phase transformations in the system $AgPO_3$–$Pr(PO_3)_3$

x^a	T_E/K^b	T_P/K^c	T_F/K^d
0.0			773
2.5	763		921
5.0	761		990
7.5	760		1025
10.0	759		1043
12.5	763		1061
15.0	762		1063
20.0	759		1099
25.0	756	1067	1170
30.0	758	1068	1197
35.0	757	1067	1245
40.0	758	1068	1285
45.0		1065	1333
50.0		1065	1355
55.0		1061	1375
60.0		1073	1399
70.0		1079	1443
80.0		1065	1477
90.0		1069	1501
100.0			1529

[a] x, mol% of $Pr(PO_3)_3$, [b] T_E, eutectic temperature, [c] T_P, peritectic temperature, [d] T_F, melting temperature

liquidus of all solid phases of the systems M^IPO_3–$Pr(PO_3)_3$ and has the general formula

$$\sum_i \nu_{io}\ln(x_i/x_{io}) = A/T + B\ln(T) + C \tag{1}$$

where ν_{io} is the stoichiometric coefficient of species i in the solid, x_{io} and x_i are the mole fractions of species i in the solid and the liquid phases, respectively, and A, B and C are constants and can be calculated by a least squares method. These constants may be expressed by the relations

$$A = (\Delta C_P T_o - \Delta H_o)/R - \alpha \tag{2}$$

$$B = \Delta C_P/R - \beta \tag{3}$$

$$C = \Delta H_o/(RT_o) - \Delta C_P(1 + \ln(T_o))/R - \gamma \tag{4}$$

R is the perfect gas constant, T_o is the stable or metastable melting point of the pure substance and ΔH_o and ΔC_p are, respectively, the variations in heat enthalpy and heat capacity of the pure substance. Coefficients α, β and γ may be expressed by an equation of the algebraic type

$$\sum_i \nu_{io}\ln(\gamma_i/\gamma_{io}) = \alpha/T + \beta\ln(T) + \gamma \tag{5}$$

where γ_i and γ_{io} are the activity coefficients of species i in the liquid and in the solid phase.

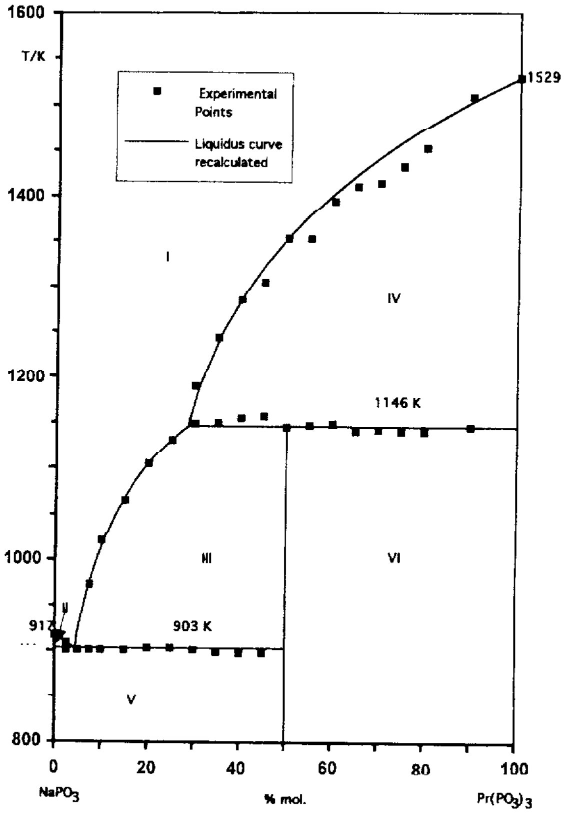

Fig. 1 Phase diagram for system $NaPO_3$–$Pr(PO_3)_3$: (I) liquid; (II) liquid+$NaPO_3$; (III) liquid+$NaPr(PO_3)_4$; (IV) liquid+$Pr(PO_3)_3$; (V) $NaPO_3$+$NaPr(PO_3)_4$; (VI) $NaPr(PO_3)_4$+$Pr(PO_3)_3$

Calculation of parameters A, B and C is carried out by using the N experimental points (xj, Tj) and minimizing the following expression:

$$Q=\sum_{j=1}^{N}\left(\sum_{i}\nu_{io}\ln(x_i/x_{io})-(A/T+B\ln(T)+C)\right)^2 \qquad (6)$$

Fitting equation

The first term of Eq. (1) can easily be expressed as a function of the composition of the liquid phase. On the assumption that the only species in the liquid phase are M^IPO_3 and $Pr(PO_3)_3$, the values of the first term of Eq. (1) for the solid phases of the systems M^IPO_3–$Pr(PO_3)_3$ are given in Table 6, where x is the mole fraction of $Pr(PO_3)_3$ in the liquid phase.

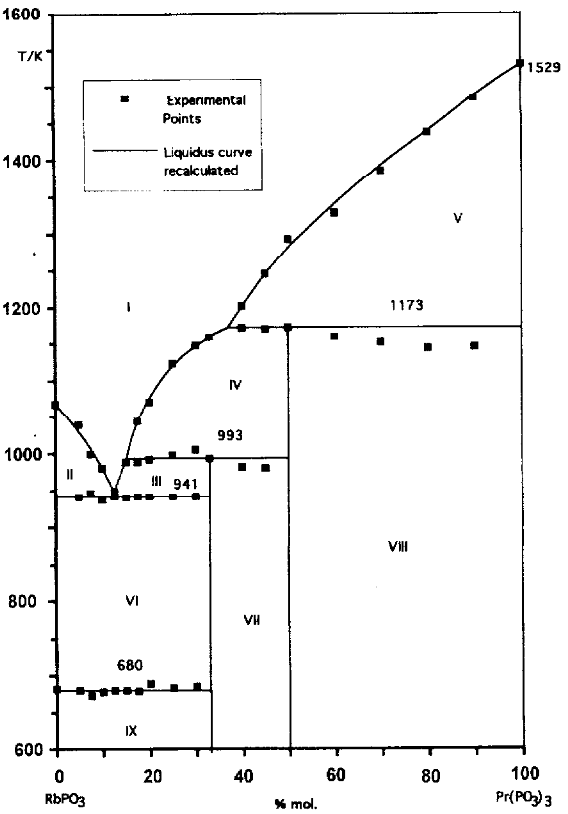

Fig. 2 Phase diagram for system $RbPO_3$–$Pr(PO_3)_3$: (I) liquid; (II) liquid+α-$RbPO_3$; (III) liquid+$Rb_2Pr(PO_3)_5$; (IV) liquid+$RbPr(PO_3)_4$; (V) liquid+$Pr(PO_3)_3$; (VI) α-$RbPO_3$+$Rb_2Pr(PO_3)_5$; (VII) $RbPr(PO_3)_4$+$Rb_2Pr(PO_3)_5$; (VIII) $RbPr(PO_3)_4$+$Pr(PO_3)_3$; (IX) β-$RbPO_3$+$Rb_2Pr(PO_3)_5$

Discussion

Analysis of the liquidus curves

The parameters of the liquidus equation for $Pr(PO_3)_3$ were calculated in each system. They aare given in Table 7.

In general, the liquidus curves of M^IPO_3 were defined by a small number of experimental values. Since the melting point T_o of a pure solid is more precisely known than the solubility determined values, the liquidus curves must pass through the points. The parameters A, B and C of the different M^IPO_3 liquidus equations are presented in Table 8.

The stoichiometries of the binary intermediate compounds found in the different systems correspond to the formula $M^I_pPr(PO_3)_{3+p}$ with p=1 or 2.

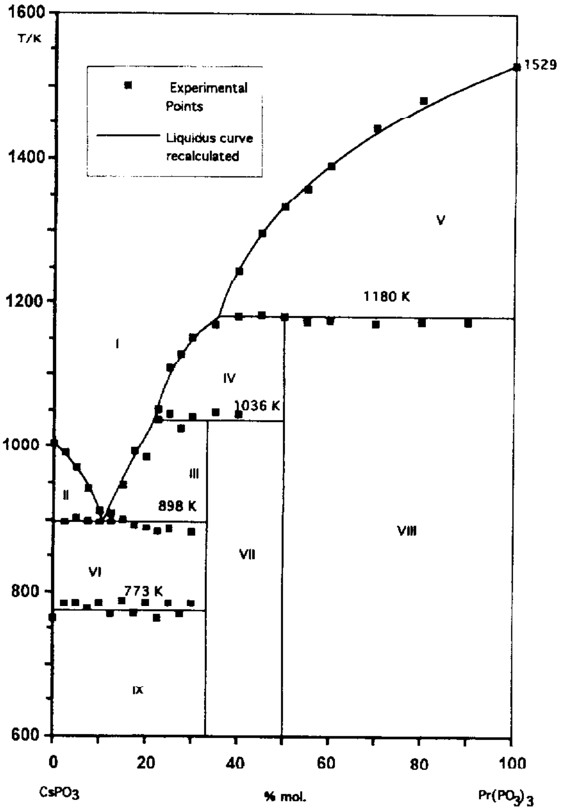

Fig. 3 Phase diagram for system $CsPO_3$–$Pr(PO_3)_3$: (I) liquid; (II) liquid+α-$CsPO_3$; (III) liquid+$Cs_2Pr(PO_3)_5$; (IV) liquid+$CsPr(PO_3)_4$; (V) liquid+$Pr(PO_3)_3$; (VI) α-$CsPO_3$+$Cs_2Pr(PO_3)_5$; (VII) $CsPr(PO_3)_4$+$Cs_2Pr(PO_3)_5$; (VIII) $CsPr(PO_3)_4$+$Pr(PO_3)_3$; (IX) β-$CsPO_3$+$Cs_2Pr(PO_3)_5$

All these solid phases undergo peritectic decomposition. Their metastable melting points were calculated and are presented in Table 9 with the parameters *A*, *B* and *C*.

Thermodynamic exploitation of liquidus curves

When the liquidus equation is known, the thermodynamic functions characteristic of stable or metastable fusion can be calculated for the ideal solution ($\alpha=\beta=\gamma=0$) from Eqs (2–4).

The values of the variation heat enthalpy of praseodymium polyphosphate thus obtained in the different systems are relatively coherent among themselves (Table 7). These calculated values are also in good agreement with those determined experimentally.

All the intermediate phases undergo peritectic decomposition on heating and their fusion was not studied further by calorimetry. The fusion thermodynamic

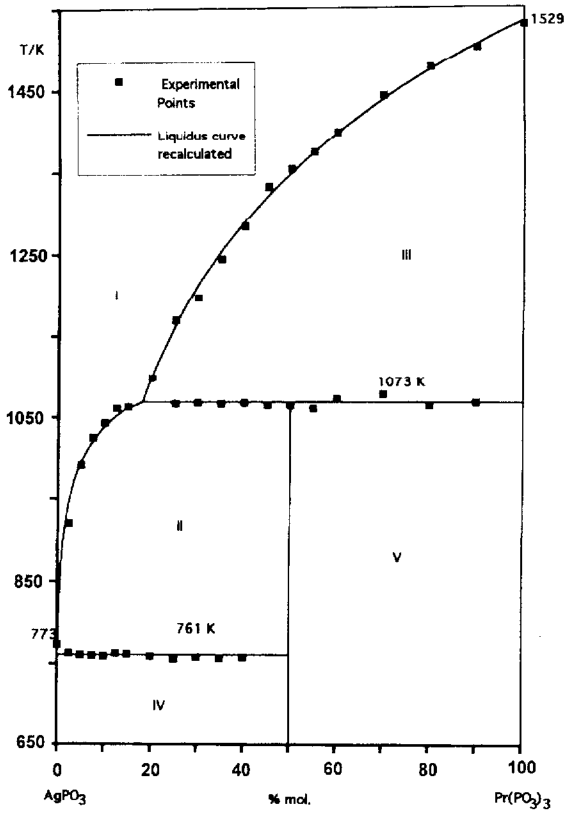

Fig. 4 Phase diagram for system $AgPO_3$–$Pr(PO_3)_3$: (I) liquid; (II) liquid+$AgPr(PO_3)_4$; (III) liquid+$Pr(PO_3)_3$; (IV) $AgPO_3$+$AgPr(PO_3)_4$; (V) $AgPr(PO_3)_4$+$Pr(PO_3)_3$

functions were calculated at the metastable melting point. The results are displayed in Table 9. These values are given only as an indication, since they are calculated on the assumption that the solution is ideal and that the liquid phase is formed by only M^IPO_3 and $Pr(PO_3)_3$.

Table 6 Systems MPO_3–$Pr(PO_3)_3$: Values of $\sum_i \nu_{io}\ln(x_i/x_{io})$

Solid phase	$\sum_i \nu_{io}\ln(x_i/x_{io})$
MPO_3	$\ln(1-x)$
$M_pPr(PO_3)_{3+p}$ (p=1, 2)	$\ln\,[x(1-x)^p(1+p)^{(1+p)}/p^p]$
$Pr(PO_3)_3$	$\ln(x)$

x, mole fraction of $Pr(PO_3)_3$

Table 7 Systems MPO_3–$Pr(PO_3)_3$: liquidus of $Pr(PO_3)_3$

Systems	ΔH_o/ kJ mol^{-1}	ΔS_o/ J K^{-1}mol^{-1}	ΔC_p/ J K^{-1}mol^{-1}	T_{fus}/K	A/K	B	C
$NaPO_3$–$Pr(PO_3)_3$	83.6	54.7	170.8	1529	21354.6	20.545	–164.61
$RbPO_3$–$Pr(PO_3)_3$	66.3	43.3	143.9	1529	18497.7	17.310	–139.02
$CsPO_3$–$Pr(PO_3)_3$	79.3	51.8	184.5	1529	24399.2	22.191	–178.67
$AgPO_3$–$Pr(PO_3)_3$	73.8	48.1	89.9	1533	7716.8	10.821	–84.41

Table 8 Systems MPO_3–$Pr(PO_3)_3$: liquidus of M^IPO_3 (M^I=Na, Rb or Cs)

M^IPO_3	ΔH_o/ kJ mol^{-1}	ΔS_o/ J K^{-1}mol^{-1}	ΔC_p/ J K^{-1}mol^{-1}	T_{fus}/K	A/K	B	C
$NaPO_3$	22.1	24.0	–0.14	917	–2665.1	–0.017	3.02
$RbPO_3$	13.5	12.6	67.95	1068	7105.1	8.173	–63.65
$CsPO_3$	14.1	14.0	113.79	1004	12056.1	13.687	–106.61

Table 9 Systems MPO_3–$Pr(PO_3)_3$: liquidus of $M_pPr(PO_3)_{3+p}$ (p=1, 2)

$M_pPr(PO_3)_{3+p}$	ΔH_{fus} kJ mol^{-1}	ΔS/ J K^{-1}mol^{-1}	ΔC_p/ J K^{-1}mol ^{1}	$T_{o\,met.}$/K	A/K	B	C
$NaPr(PO_3)_4$	65.7	55.6	52.9	1181	–386.2	6.36	–44.71
$RbPr(PO_3)_4$	55.3	46.7	211.1	1184	23411.6	25.38	–199.40
$CsPr(PO_3)_4$	36.18	29.85	140.5	1212	16131.0	16.90	–133.29
$Cs_2Pr(PO)_5$	34.16	32.01	79.45	1067	6086.3	9.55	–73.42
$AgPr(PO_3)_4$	145.4	131.0	215.6	1110	11298.2	25.93	–192.04

The liquidus study of the polyphosphates M^IPO_3 was limited to the Na, Rb and Cs salts, whose experimental liquidus curves were sufficiently well defined to allow a thermodynamic exploitation. Given the precision and the number of experimental determinations, the calculated values of heat enthalpy (Table 8) agree with the experimental ones.

Conclusions

A semi-empirical equation of the liquidus curve already established for the binary water–salt systems was applied with success to salt–salt systems: M^IPO_3–$Pr(PO_3)_3$ (M^I=Na, Rb, Cs or Ag).

This equation is useful for an intermediate or limit phase in the complete range of temperatures and compositions. The analytical expression obtained perfectly describes the experimental liquidus curves of all the solid phases in the systems M^IPO_3–$Pr(PO_3)_3$. Moreover, the metastable melting points of intermediate phases were determined. The thermodynamic function characteristic of the fusion was calculated with a simplified hypothesis for all the solid phases whose experimental liquidus curves have been determined. Comparison of the measured and calculated values of heat enthalpies of M^IPO_3 and $Pr(PO_3)_3$ demonstrates that they are in concordance.

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