Equilibrium diagram of KPO_3–$Y(PO_3)_3$ system, chemical preparation and characterization of $KY(PO_3)_4$

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Abstract

Microdifferential thermal analysis (μ-DTA), X-ray diffraction (XRD) and infrared (IR) spectroscopy were used for the first time to investigate the liquidus and solidus relations in the KPO_3–$Y(PO_3)_3$ system. The only compound observed within the system was $KY(PO_3)_4$ melting incongruently at 1033 K. An eutectic appears at 13.5 mol% $Y(PO_3)_3$ at 935 K, the peritectic occurs at 1033 K and the phase transition for potassium polyphosphate KPO_3 was observed at 725 K. Three monoclinic allotropic phases of the single crystals were obtained. $KY(PO_3)_4$ polyphosphate has the $P2_1$ space group with lattice parameters: $a = 7.183(4)$ Å, $b = 8.351(6)$ Å, $c = 7.983(3)$ Å, $\beta = 91.75(3)°$ and $Z = 2$ is isostructural with $KNd(PO_3)_4$. The second allotropic form of $KY(PO_3)_4$ belongs to the $P2_1/n$ space group with lattice parameters: $a = 10.835(3)$ Å, $b = 9.003(2)$ Å, $c = 10.314(1)$ Å, $\beta = 106.09(7)°$ and $Z = 4$ and is isostructural with $TlNd(PO_3)_4$. The IR absorption spectra of the two forms show a chain polyphosphates structure. The last modification of KYP_4O_{12} crystallizes in the $C2/c$ space group with lattice parameters: $a = 7.825(3)$ Å, $b = 12.537(4)$ Å, $c = 10.584(2)$ Å, $\beta = 110.22(7)°$ and $Z = 4$ is isostructural with $RbNdP_4O_{12}$ and contains cyclic anions. The methods of chemical preparations, the determination of crystallographic data and IR spectra for these compounds are reported.
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1. Introduction

The fluorescence and laser properties of phosphate hosts of doped rare-earth materials are well known and investigation of such materials has attracted many scientists [1–3]. Extensive study has been carried out on the rare-earth tetra- and ultraphosphates [4,5]. Phase diagrams play important roles in interpreting the variation of properties with composition. The systematic investigation of new long chain polyphosphates containing monovalent and trivalent cations, appearing in the $M^I PO_3$–$M^{III}(PO_3)_3$ systems (M^I: monovalent cation, M^{III}: rare-earth trivalent cation, Bi and Y) [6–8], and especially the KPO_3–$M^{III}(PO_3)_3$ systems (M^{III} = La [9,10], Ce [11,12], Sm [13], Er [14], Bi [15]) as a possible basis for producing inorganic materials is promising. In this work we report, for the first time, the results obtained for the KPO_3–$Y(PO_3)_3$ system. The preparation, the crystallographic data and the spectroscopic properties of the three allotropes of the double

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potassium yttrium polyphosphate $KY(PO_3)_4$ are described. Our future aim is to study the ionic conductivity and the optical properties of such materials.

2. Experimental

2.1. Preparation of samples

Potassium and yttrium polyphosphate were individually prepared in our laboratory to establish the solid–liquid equilibrium diagram of the KPO_3–$Y(PO_3)_3$ system. KPO_3 was made by heating recrystallized KH_2PO_4, in a platinum crucible, until all water was driven off, then treated at 1273 K for 1 h, and then recrystallized by heat treating at 973 K for 2 days [16]. Sodium cyclotriphosphate $Na_3P_3O_9$ was prepared by heating sodium dihydrogenophosphate dihydrate $NaH_2PO_4 \cdot 2H_2O$ (MERCK, purified by recrystallization) at 1073 K for 1 h. The resulting vitreous liquid was cooled on a metallic plate and then ground to a fine powder. Crystallized $Na_3P_3O_9$ was then obtained after annealing for 12 h at 673 K. $Y(PO_3)_3$ was made by complete dehydration of yttrium cyclotriphosphate pentahydrate $YP_3O_9 \cdot 5H_2O$ at 450 K. $YP_3O_9 \cdot 5H_2O$ was prepared at room temperature by mixing, under mechanical stirring, aqueous 0.1 M solutions of $YCl_3 \cdot 6H_2O$ and $Na_3P_3O_9$ in a 1:1 ratio. The stirring was continued for 2 days until a white precipitate was obtained. The product was filtered, washed with hot water and dried in air. The reaction is given in Eq. (1) [17]

$$Na_3P_3O_9 + YCl_3 \cdot 6H_2O$$
$$\rightarrow YP_3O_9 \cdot 5H_2O + 3NaCl + H_2O \qquad (1)$$
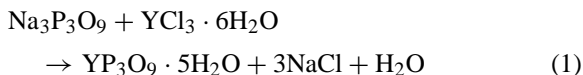
The samples for investigations were prepared by mixing appropriate ratios of potassium and yttrium polyphosphates KPO_3 and $Y(PO_3)_3$. The compounds were mixed at the desired compositional ratios, where the molar fraction of $Y(PO_3)_3$ varies from 0 to 90% with intervals of 2.5, 5 and 10%. The homogeneity of samples were assured by frequent grinding in an agate mortar, then each mixture was reacted in platinum crucibles for 5 days at 573 K. Pellets were cold-pressed, then heat treated at 723 K for 10 days. The $Y(PO_3)_3$ rich mixtures were further heated at 923 K.

2.2. Technical characterization

The equilibrium diagram of the binary system KPO_3–$Y(PO_3)_3$ was established using the following techniques.

2.2.1. Microdifferential thermal analysis (μ-DTA)

The (μ-DTA) traces of the samples were measured using a RIGAKU 821202 A 36 apparatus in recording the heating curves of materials up to the melting temperature in platinum crucibles under an air atmosphere. All samples were almost of the same mass ($\cong$1 g). Pt/Pt–Rh (13%) thermocouple (calibrated against the melting point of NaCl, 1077 K and the transition and melting points of K_2SO_4 at 856 and 1342 K, respectively) was used to detect thermal phenomena. The heating rate of the furnace was 10 K/min and α-Al_2O_3 powder was used as reference material.

2.2.2. X-ray diffraction (XRD)

The initial components and the new compounds formed in the system were identified by XRD on a PHILIPS PW 1730 diffractometer with Cu $K_{\alpha 1}$ radiation ($\lambda = 1.54056$ Å). The recording speed was ((1/8)°/min/2θ).

2.2.3. Infrared (IR) spectroscopy

Solid pellets were prepared using a mixture of 2 mg of the sample with 300 mg of pure dried KBr. The IR absorption spectra were recorded in the range of 4000–400 cm^{-1} using the Perkin Elmer spectrometers, FTIR783, and FTIR spectrum 1000.

3. Results and discussion

3.1. Equilibrium diagram of KPO_3–$Y(PO_3)_3$

The results of the thermal analysis gave the phase equilibrium diagram of the system which is shown in Fig. 1. The system shows that one phase, $KY(PO_3)_4$, at 50 mol% $Y(PO_3)_3$ is formed, which melting incongruently on heating at 1033 K, as described in Eq. (2)

$$KY(PO_3)_4 \rightarrow Y(PO_3)_3 + \text{liquid} \qquad (2)$$
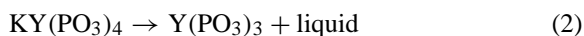
The branches of the liquidus curve intersect the monovariant peritectic line at 19 mol% $Y(PO_3)_3$. The line at 725 K corresponds to the polymorphic reversible
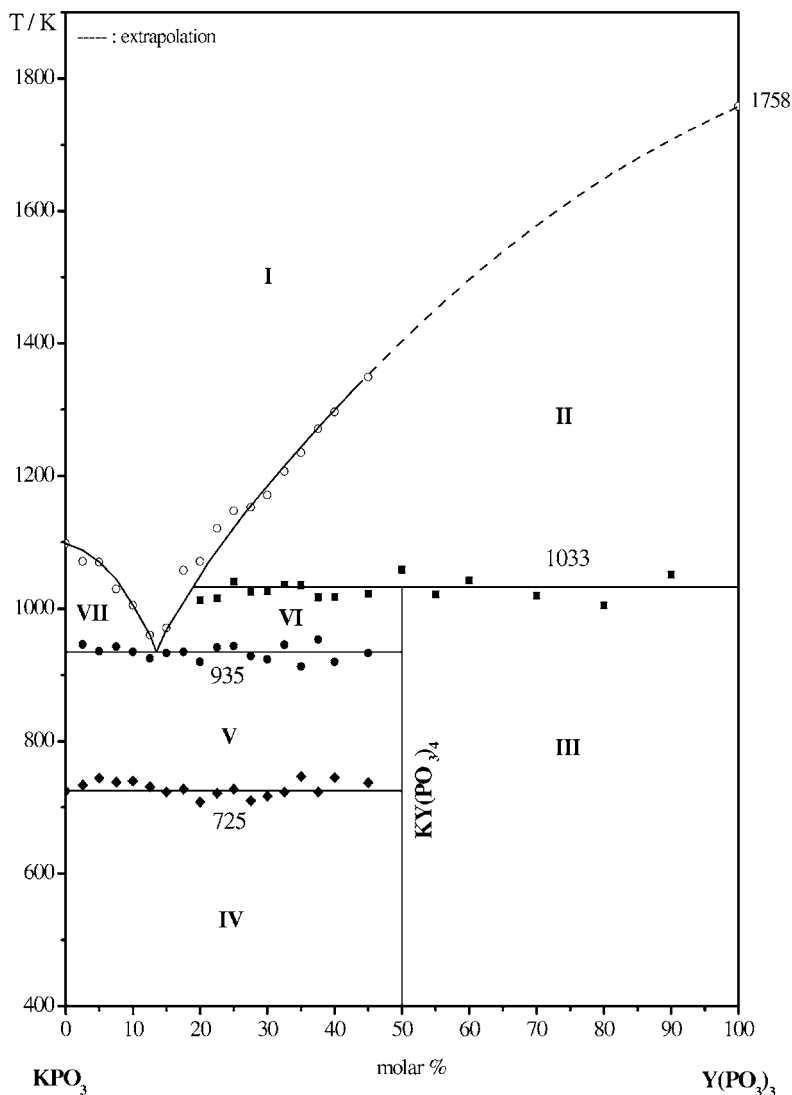
Fig. 1. Phase diagram of the KPO_3–$Y(PO_3)_3$ system. (I) Liquid; (II) $Y(PO_3)_3$+liquid; (III) $KY(PO_3)_4$+$Y(PO_3)_3$; (IV) $KPO_3(\beta)$+$KY(PO_3)_4$; (V) $KPO_3(\alpha)$ + $KY(PO_3)_4$; (VI) $KY(PO_3)_4$ + liquid; (VII) $KPO_3(\alpha)$ + liquid.

transformation of potassium polyphosphate (Eq. (3)) [9–16]

$$\beta\text{-}KPO_3 \leftrightarrows \alpha\text{-}KPO_3 \tag{3}$$

The eutectic invariant occurs at 935 K and the line is situated between 0 and 50 mol% $Y(PO_3)_3$. The eutectic point is found at 13.5 mol% $Y(PO_3)_3$. This composition is in accordance with the Tamman's triangle constructed from the μ-DTA data. For temper-

atures above 1400 K. The melting temperatures were obtained by extrapolating to the melting temperature of $Y(PO_3)_3$ at 1758 K, taken from Ref. [7].

3.2. Chemical preparation of $KY(PO_3)_4$

$KY(PO_3)_4$ was prepared by the following methods:

(i) Stoichiometric mixture of KPO_3 and $Y(PO_3)_3$. A stoichiometric mixture of 50 mol% of potassium

Table 1
Crystallographic parameters of the three allotropic phases of $KY(PO_3)_4$

Phases	Space group	Parameters (Å)	β (°)	Z
$KY(PO_3)_4$	$P2_1$	$a = 7.183(4)$, $b = 8.351(6)$, $c = 7.983(3)$	91.75(3)	2
$KY(PO_3)_4$	$P2_1/n$	$a = 10.835(3)$, $b = 9.003(2)$, $c = 10.314(1)$	106.09(7)	4
KYP_4O_{12}	$C2/c$	$a = 7.825(3)$, $b = 12.537(4)$, $c = 10.584(2)$	110.22(7)	4

and yttrium polyphosphate (KPO_3 and $Y(PO_3)_3$) first heated at 573 for 1 week and then calcined for several days at 773 K, gives the $P2_1/n$ form of $KY(PO_3)_4$.

(ii) Stoichiometric mixture of K_2CO_3, Y_2O_3 and $(NH_4)_2HPO_4$. The $P2_1/n$ form of $KY(PO_3)_4$ sample can be obtained also by melting together potassium carbonate, yttrium oxide and diammonium hydrogen phosphate in the 1:1:8 molar ratio as described in Eq. (4)

$$K_2CO_3 + Y_2O_3 + 8(NH_4)_2HPO_4 \rightarrow 2KY(PO_3)_4 + 16NH_3 + CO_2 + 12H_2O \qquad (4)$$
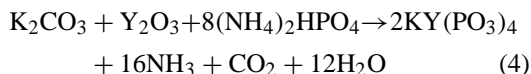
The initial components were thoroughly ground and slowly heated at 573 K until all gases were removed and the material fused together. Then the mixture was calcined for several days at 773 K.

(iii) Crystal growth by the flux method. Homogeneous solution of potassium carbonate K_2CO_3 (6 g) and yttrium oxide Y_2O_3 (0.5 g) containing a large excess of orthophosphoric acid H_3PO_4 (10 ml, 85% concentration) was heated in a vitreous carbon crucible at 473 K for 1 day. Then the temperature of the furnace was slowly raised to the predermined temperature in the range of 573–623 K for 7 days. After cooling, crystals are washed with a hot solution of a nitric acid. This method gives a mixture of three polymorphics phases $P2_1$, $P2_1/n$ and $C2/c$.

3.3. Crystal data

We established the individuality of the obtained modifications by XRD analysis and IR spectroscopy. The examination of the XRD pattern and the vibrational spectra for separated and ground crystals of the specimens shows the existence of three polymorphic phases. The parameters obtained by the refinement

of the X-ray data using the least squares method are reported in Table 1. The examination of the crystallographic data shows that these phases are isostructural with homologues $M^I Ln(PO_3)_4$ or $M^I LnP_4O_{12}$ with known crystals structures. Preparation of single crystals of $KY(PO_3)_4$ gave three monoclinic allotropes. $KY(PO_3)_4$ polyphosphate with the $P2_1$ space group is isostructural with $KNd(PO_3)_4$ [18,19]. The second allotropic form of $KY(PO_3)_4$ belongs to $P2_1/n$ space group, and is isostructural with $TlNd(PO_3)_4$ [20]. In these two forms the phosphate anion has a chain structure. KYP_4O_{12} which crystallizes in the $C2/c$ space group is isostructural with $RbNdP_4O_{12}$ [21]. The structure is built from $P_4O_{12}{}^{4-}$ cyclotetraphosphate anions linked by YO_8 polyhedra to a three-dimensional framework, in the intersecting tunnels the K^+ ions are located. The P_4O_{12} anion is centrosymmetric [22].

3.4. IR spectra

The IR spectra of the three phases, recorded in the interval $4000–400\,cm^{-1}$ are shown in Fig. 2. The observed frequencies of the different vibrations are presented in Table 2. The IR spectra of the $P2_1$ (Fig. 2a) and $P2_1/n$ (Fig. 2b) allotropic forms of $KY(PO_3)_4$ show the following bands, characteristic of linear phosphate [12,23,24]:

(i) ν_{as} OPO^- between 1310 and $1240\,cm^{-1}$; ν_s OPO^- between 1180 and $1020\,cm^{-1}$.

(ii) ν_{as} POP between 1030 and $890\,cm^{-1}$; ν_s POP between 790 and $660\,cm^{-1}$.

(iii) δ OPO^-, δ POP and ν MO at frequencies below $625\,cm^{-1}$, this group of absorptions is typical of chain polyphosphates.

One of the most noteworthy features of the spectrum presented in Fig. 2c, corresponding to the $C2/c$ form of KYP_4O_{12} cyclotetraphosphate is the appear-
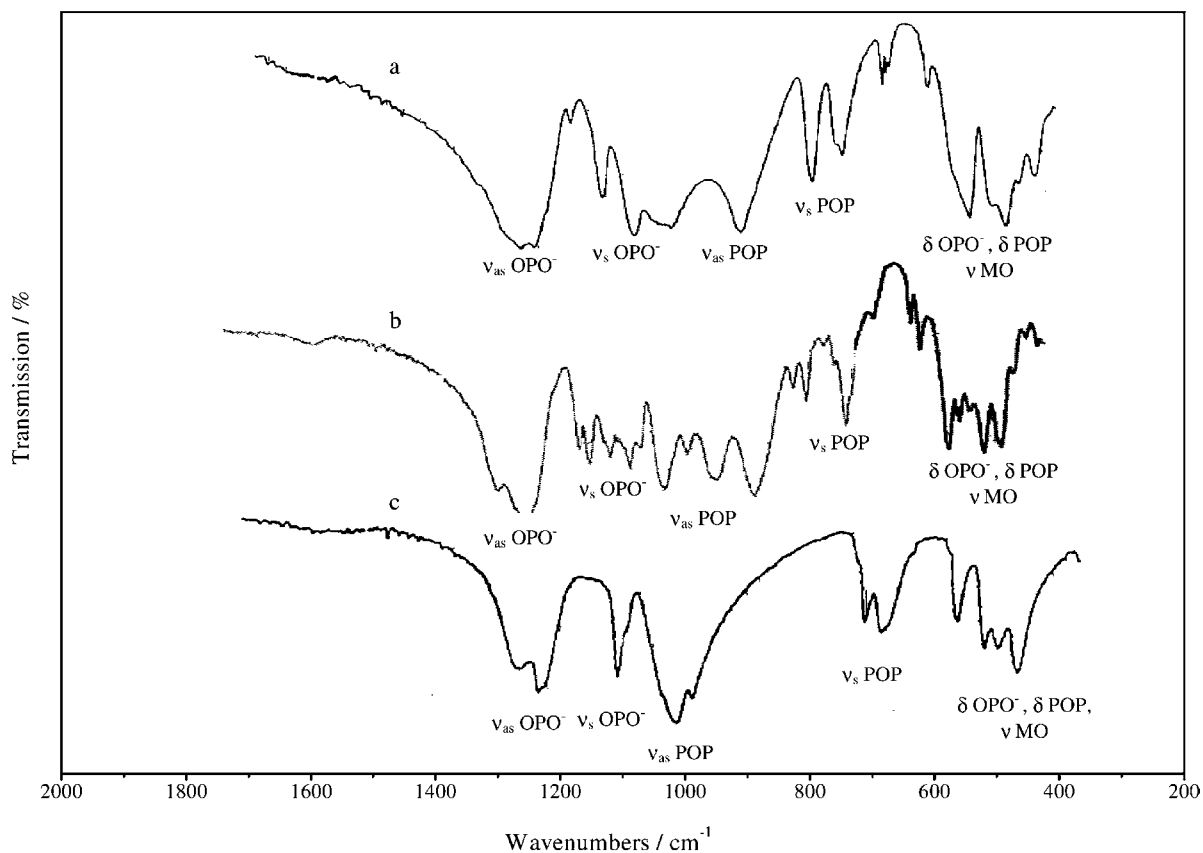
Fig. 2. FTIR spectrum of three allotropic forms of $KY(PO_3)_4$: (a) $P2_1$; (b) $P2_1/n$; (c) $C2/c$.

Table 2
Mode frequencies (cm^{-1}) in the three allotropic phases of $KY(PO_3)_4$

Assignment	$KY(PO_3)_4$ ($P2_1$)	$KY(PO_3)_4$ ($P2_1/n$)	KYP_4O_{12} ($C2/c$)
ν_{as} OPO$^-$	1265–1240	1312–1262	1280–1250–1240
ν_s OPO$^-$	1180–1130–1082–1020	1178–1160–1125–1090	1125–1115–1050–1025
ν_{as} POP	910	1035–998–950–888	1005
ν_s POP	792–742–675–670–665	820–800–770–735	800–735–710–700
δ OPO$^-$, δ POP and ν MO	602–540–505–482–460–432	625–610–565–548–530–508–480–455–430–415	588–542–520–485

ance of very strong absorption bands at 1280–1240, 1125–1110, 1050–1025 and 800–700 cm^{-1}, which can be assigned ν_{as} OPO$^-$, ν_s OPO$^-$, ν_{as} POP and ν_s POP vibrations, respectively [23,25]. The presence of a very strong broad absorption band near 1000 cm^{-1} is also a distinguishing feature of this compound [23].

4. Conclusion

The KPO$_3$–Y(PO$_3$)$_3$ system was studied for the first time. μ-DTA, XRD and IR spectroscopy were used to investigate the liquidus and solidus relations in this system. The only compound observed in the system was $KY(PO_3)_4$ melting incongruently at 1033 K.

Three allotropic phases of the $KY(PO_3)_4$, with the space groups $P2_1$, $P2_1/n$ and $C2/c$ were isolated and characterized.

References

[1] T. Yamada, K. Otsuka, J. Nakano, J. Appl. Phys. 45 (1974) 5097.

[2] K. Horchani, J.C. Gâcon, C. Dujardin, N. Garnier, C. Garapon, M. Férid, M. Trabelsi-Ayadi, J. Lumin. 94–95 (2001) 69.

[3] A. Jouini, J.C. Gâcon, A. Brenier, M. Férid, M. Trabelsi-Ayadi, J. Lumin. (2002), in press.

[4] M. Malinowski, B. Jackier, G. Boulon, W. Wolinski, J. Lumin. 39 (1988) 301.

[5] H. Kanno, Y. Akama, J. Alloys Compd. 250 (1997) 528.

[6] A. Jouini, M. Férid, M. Trabelsi-Ayadi, Mater. Res. Bull. (2002), submitted for publication.

[7] E.N. Fedorova, L.K. Shmatok, I.I. Kozina, G.R. Barabanova, Inorg. Mater. 22 (1986) 480.

[8] W. Szuszkiewicz, Mater. Chem. Phys. 38 (1994) 87.

[9] M. Férid, N.K. Ariguib, M. Trabelsi, Mater. Chem. Phys. 10 (1984) 25.

[10] D. Ben Hassen, N.K. Ariguib, M. Trabelsi-Ayadi, R. Tenu, J.J. Counioux, Thermochim. Acta 116 (1987) 85.

[11] M. Rzaigui, M. Dabbabi, N.K. Ariguib, J. Chim. Phys. 78 (6) (1981) 563.

[12] I.V. Mardirosova, M.M. Ali, G.A. Bukhalova, Izv. Akad. Nauk. SSSR, Neorg. Mater. 20 (1984) 292.

[13] M. Férid, N.K. Ariguib, M. Trabelsi-Ayadi, J. Solid State Chem. 69 (1987) 1.

[14] M. Férid, N.K. Ariguib, M. Trabelsi-Ayadi, Thermochim. Acta 136 (1988) 139.

[15] G.A. Bukhalova, R.S. Faustova, M.A. Savenkova, Zh. Prikl. Khim. 50 (1977) 171.

[16] G.W. Morey, J. Am. Chem. Soc. 76 (1954) 4724.

[17] A. Jouini, M. Férid, M. Trabelsi-Ayadi, Montpelllier, Journées d'Etude d'Equilibres Entre Phases XXVII JEEP (2001) 13.

[18] K.K. Palkina, V.G. Kusnetsov, N.N. Chudinova, N.T. Chibiskova, Izv. Akad. Nauk. SSSR, Neorg. Mater. 12 (1976) 730.

[19] H.Y.-P. Hong, Mater. Res. Bull. 10 (1975) 1105.

[20] K.K. Palkina, V.Z. Saifuddinov, V.G. Kuznetsov, N.N. Chudinova, Sov. Phys. Dokl. 22 (1977) 698.

[21] H. Koizumi, J. Nakano, Acta Cryst. B 33 (1977) 2680.

[22] A. Hamady, T. Jouini, A. Driss, Acta Cryst. C 51 (1995) 1970.

[23] D.E. Corbridge, E.J. Lowe, J. Chem. Soc. (1954) 493.

[24] N.N. Chudinova, N.V. Vinogradova, Izv. Akad. Nauk. SSSR, Neorg. Mater. 15 (1979) 2171.

[25] G. Foumakoye, R. Cahay, P. Tarte, Spectrochim. Acta 8 (1990) 1245.