Phase equilibria in the $\text{ErPO}_4\text{--KPO}_3$ system

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Received: 29 June 2015 / Accepted: 25 August 2015 / Published online: 8 September 2015
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Abstract The phase equilibria occurring in the $\text{ErPO}_4\text{--KPO}_3$ system were investigated by thermoanalytical, X-ray powder diffraction and FTIR methods. On the basis of the obtained results, its phase diagram was proposed. This system includes one intermediate compound, KErP_2O_7 . This phosphate decomposes peritectically at about 1025 °C and occurs in two polymorphic forms; transformation $\beta/\alpha\text{-KErP}_2\text{O}_7$ proceeds at about 358 °C. The binary erbium end potassium diphosphate, KErP_2O_7 , was obtained by the ceramic and modified Pechini methods. Structural properties were characterized by X-ray powder diffraction and FTIR spectroscopy.

Keywords Phase diagram · Erbium and potassium diphosphate · DSC · DTA/TG/DTG · XRD

Introduction

For the last few decades, double diphosphates of a general formula $M^I\text{LnP}_2\text{O}_7$ ($M^I = \text{Li, Na, K, Rb, Cs, Tl, Ag}$; $M^{\text{III}} = \text{Al, Ga, In, Fe, Sc, Y, Ln, transition metal}$) have attracted considerable interest [1–19]. It has been primarily focused on the crystal structure, synthesis methods and prospective practical applications. These compounds are

mainly obtained in the solidstate reaction by annealing various mixtures at different temperature and time range. As starting reaction mixtures the following compositions were used:

1. Ln_2O_3 and $M^I\text{PO}_3$ using a large amount of an alkali metaphosphate, the excess of which was washed away with hot water, sometimes with lithium chloride [1–4]; the annealing was carried out in the temperature range 550–750 °C.
2. Stoichiometric amounts of substrate phosphates LnPO_4 and $M^I\text{PO}_3$; the synthesis was carried out in the temperature range 400–900 °C [5–8].
3. Carbonates or nitrates of alkali metals $M_2^I\text{CO}_3/M^I\text{NO}_3$, Ln_2O_3 and $(\text{NH}_4)_2\text{HPO}_4$; the synthesis proceeded in the temperature range 400–1200 °C [9–18].

A review of the literature shows that double diphosphates in the pure phase form as well as doped with various ions (mainly Ln) have interesting optical and dielectric properties, which indicates the nature of the applications as scintillators or phosphor materials based on $A^I M^{\text{III}}\text{P}_2\text{O}_7$ -type diphosphates [16–23] or as ionic conductors [2, 4, 11]. These compounds have diverse crystal structures. They crystallize in the following systems: a monoclinic (lowtemperature form, various SG), an orthorhombic (hightemperature form; various SG), a hexagonal (the highest temperature form for Y, Tb, Dy and Er, but crystallographic data have not been given [1, 9]) and a tetragonal (pseudo-pyrophosphate-type PPP) [15]. It has been found that the formation of $M^I M^{\text{III}}\text{P}_2\text{O}_7$ double diphosphates and their crystal structures depend on the ionic radii ratio r_M^I/r_M^{III} [9–11]. According to [1] the thermal stability of the compounds, where $M^I = \text{K, Rb, Cs}$ and $M^{\text{III}} = \text{Tb–Lu}$, increases with the alkali metal atomic number (i.e. in the series K–Rb–Cs), and as the lanthanide

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atomic number increases. They melt incongruently forming LnPO_4 [1].

Double diphosphates, according to their stoichiometric composition, should be present in systems of the $\text{LnPO}_4\text{--}M\text{PO}_3$ type, in the molar ratio of the starting compounds equal 1:1. Determination of the phase relationships in such systems, particularly in the entire range of temperature and composition, is relevant because it leads to discovery of new phases and also allows to determine their physicochemical properties. Our research team has developed phase diagrams of the following systems: $\text{LnPO}_4\text{--KPO}_3$ (where: $\text{Ln} = \text{La}, \text{Ce}, \text{Nd}, \text{Y}$), $\text{LnPO}_4\text{--NaPO}_3$ (where: $\text{Ln} = \text{Ce}, \text{Nd}, \text{Y}$) [5–9, 24–26]. It turned out that for $M = \text{K}$, double diphosphate of formula KYP_2O_7 , only occurs in the $\text{YPO}_4\text{--KPO}_3$ system. It melts incongruently at 1000 °C according to the reaction: $\text{KYP}_2\text{O}_7 \rightarrow \text{YPO}_4 + \text{liquid}$. In the other $\text{LnPO}_4\text{--KPO}_3$ systems the compounds are not formed; these are simple systems of an eutectic type whereas in $\text{LnPO}_4\text{--NaPO}_3$ systems double diphosphates are formed only for $\text{Ln} = \text{Ce}$ and Nd . These are NaCeP_2O_7 and NaNdP_2O_7 . In the $\text{YPO}_4\text{--NaPO}_3$ system $\text{Na}_2\text{YP}_3\text{O}_{10}$ tripolyphosphate is formed; it corresponds to the molar ratio of the starting components $\text{YPO}_4\text{:NaPO}_3 = 1\text{:}2$. Three mentioned above compounds melt incongruently at 800 (Ce), 790 (Nd) and 640 °C (Y), respectively, giving the corresponding lanthanide orthophosphate LnPO_4 and liquid.

This paper presents the results of investigations of the phase equilibria in the $\text{ErPO}_4\text{--KPO}_3$ system. Its phase diagram is not known. In the literature, there are numerous reports on the starting phosphates, i.e. ErPO_4 and KPO_3 . It is known that both compounds melt congruently at 1896 ± 20 °C [27, 28] and 810 ± 20 °C [29], respectively. Their polymorphism has been investigated by plenty of authors (see, e.g. [28–33]). Erbium orthophosphate ErPO_4 , is related to the LnPO_4 group with xenotime structure, isostructural to zircon (ZrSiO_4) and it crystallizes in the tetragonal system [SG I41/amd, $a = 6.8614(5)$, $c = 6.0082(9)$ Å, $Z = 4$] [33]. ErPO_4 exists in one polymorphic form [30].

Potassium metaphosphate KPO_3 melts congruently at 810 °C and, as the other alkali metal metaphosphates, tends to solidify not into a crystalline but into a glass form. It undergoes two polymorphic transformations: α/β at 449 °C and β/γ at 665 °C [29]. Decomposition of the compound begins only in the liquid phase at 1160 °C [33] (i.e. substantially above the melting point).

It is known from the literature that KErP_2O_7 exists. According to [9], the compound crystallizes in the orthorhombic system [$a = 9.198(8)$, $b = 12.209(8)$, $c = 5.698(5)$ Å] whereas from [1], this diphosphate occurs in three polymorphic modifications: the low-temperature one (type I) crystallizes in the monoclinic system

[$a = 7.5670(3)$, $b = 10.9090(3)$, $c = 8.5830(3)$ Å and $\beta = 106.84(3)^\circ$] PDF 00-049-0766, the orthorhombic system (type III) [$a = 9.1950(3)$, $b = 12.2160(5)$, $c = 5.7040(1)$ Å] PDF 00-049-0767, and the high-temperature hexagonal system (type IV) [$a = 9.5530(3)$, and $c = 12.6380(4)$ Å] PDF 00-049-0768. The polymorphic transformation from the monoclinic to the orthorhombic form in KErP_2O_7 takes place in the temperature range 350–370 °C [1], but the temperature of the next polymorphic transformation (the orthorhombic to the hexagonal) is not known. The $\text{KErP}_2\text{O}_7(\text{III}) \leftrightarrow \text{KErP}_2\text{O}_7(\text{IV})$ transformation is reversible. However, rapid cooling of $\text{KErP}_2\text{O}_7(\text{IV})$ from high temperature do not completely convert it into $\text{KErP}_2\text{O}_7(\text{III})$ [1].

Experimental

Materials and samples preparation

The following commercial materials: Er_2O_3 (99.9 %, Aldrich), and $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, KNO_3 , K_2CO_3 , KH_2PO_4 (POCh)—all analytically pure were used to prepare the test samples from the $\text{ErPO}_4\text{--K}_3\text{PO}_4$ system. The erbium orthophosphate ErPO_4 was synthesized from Er_2O_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ by the method described in [34]. Potassium phosphate KPO_3 was obtained KH_2PO_4 by dehydration at 350 °C for 2 h.

Samples for investigations were presynthesized by the reaction in the solid phase. The substrates were weighed out in fixed amounts, thoroughly mixed, rubbed in an agate mortar, and then sintered. The sintering temperature and time were determined experimentally.

Physicochemical characterization

Phase equilibria in the $\text{ErPO}_4\text{--KPO}_3$ system were investigated by thermoanalytical methods DTA/TG/DSC, X-ray powder diffraction XRD and FTIR spectroscopy.

The DSC/TG analysis during heating carried out by using a calorimeter SETSYSTM (TG-DSC 1500; SETA RAM) up to 1300 °C (heating rate: 10 K min^{-1} , argon atmosphere, platinum crucibles; mass of samples 15–30 mg). The DTA/TG heating was performed by means of a derivatograph type 3427 (MOM, Hungary) within temperature range of 20–1400 °C with a heating rate $5 \text{ }^\circ\text{C min}^{-1}$. Platinum crucibles and an air atmosphere were used; mass of samples was 400–600 mg. The standard substance was Al_2O_3 . The temperatures were measured by a Pt/PtRh10 thermocouple standardized for the melting points of NaCl (801 °C), K_2SO_4 (1070 °C), $\text{Ca}_2\text{P}_2\text{O}_7$ (1353 °C) and the transition points of K_2SO_4 (583 °C). The high-temperature experiments were also conducted in a

horizontal resistance furnace with molybdenum winding, under argon. Presynthesized samples of about 3 g mass were pressed into pellets and placed in boats made of PtRh30 alloy. Temperature points at which the samples began to melt and disappeared from the visual field were read with an optical pyrometer. For the samples that melt in a range of temperature, the points determined are approximate. The optical pyrometer was calibrated against the melting points of $\text{Ca}_2\text{P}_2\text{O}_7$ (1353 °C), Na_3PO_4 (1583 °C) and $\text{Ca}_3(\text{PO}_4)_2$ (1810 °C).

The X-ray powder diffraction (XRD) was used to determine the phase composition of final powders. The phase analysis was made using D5000 diffractometer (Siemens, Germany). The $\text{CuK}\alpha$ radiation ($\lambda = 0.154$ nm) was applied in measurements at room temperature in an angle range of 2θ : 10°–60° with 2θ scanning speed $0.04^\circ \text{ s}^{-1}$ and count-time of 2 s/step.

The high temperature (up to 950 °C) of X-ray diffraction (XRD) method with DRON-2 diffractometer using Felfiltered $\text{CoK}\alpha$ X-ray beam ($\lambda = 0.179$ nm) was taken for identification the crystal phases in examined samples. The diffraction was taken in 2θ range of 15°–45° and in a scan mode of step recording every $\Delta 2\theta = 0.05^\circ$. The crystal structure of the samples was identified using XRayan program by comparing the interplanar crystal spacing d and intensities of reflections I of the investigate samples with powder diffraction files (PDF) data. The quantity analysis and the crystallite sizes were calculated using RTG-3 program.

The infrared spectra at room temperature were measured in the spectral range 400–4000 cm^{-1} using a FTIR Biorad 575C Spectrometer. The samples were prepared in KBr pellet suspension. The spectral resolution was 2 cm^{-1} .

Results and discussion

Phase equilibria occurring in the $\text{ErPO}_4\text{--KPO}_3$ system have been investigated over the entire range of composition, up to 1800 °C, by DTA/TG/DSC thermoanalytical methods, powder X-ray diffraction (XRD), and FTIR spectroscopy.

The experimental work started with obtaining KErP_2O_7 diphosphate in the pure phase form. For this purpose, various substrates and various synthesis conditions were applied (Table 1). Attempts to obtain pure phase KErP_2O_7 in the reaction of ErPO_4 with KPO_3 (Table 1, sample S1) failed. The starting phosphates were not reactive at lower temperature, the samples were always a mixture of ErPO_4 and KPO_3 , and at 800 °C—a mixture of KErP_2O_7 and ErPO_4 .

The methods used for samples S2–S6 (Table 1) yielded pure phase KErP_2O_7 . However, its crystallographic structure depended on the applied temperature during heat

treatment. In Fig. 1 XRD patterns of the samples S2–S6 (Table 1) at room temperature (SIEMENS D5000) are presented. In the diffraction patterns of the samples S2, S3 and S5 reflections characteristic of the $\beta\text{-KErP}_2\text{O}_7$ monoclinic structure (PDF 00-049-0766) are visible, whereas XRD patterns of the samples S4 and S6 are characteristic of the orthorhombic $\alpha\text{-KErP}_2\text{O}_7$ structure (PDF 00-049-0767).

Figure 2 presents infrared spectra of the products obtained by solidstate reaction (samples S2–S4) and Pechini method (S5 and S6). FTIR spectroscopic studies in the range 400–1400 cm^{-1} confirmed the phase purity of the obtained KErP_2O_7 . It is known from the literature reports concerning spectroscopic research on double diphosphates of $A^{\text{I}}M^{\text{III}}\text{P}_2\text{O}_7$ type that the bands characteristic for $(\text{P}_2\text{O}_7)^{4-}$ group are present in the wavenumber ranges: 1080–1250, 975–1070, 910–950, 720–750 and 370–680 cm^{-1} and they are assigned respectively to the vibrations: $\nu_{\text{as}}(\text{PO}_3)$, $\nu_{\text{s}}(\text{PO}_3)$, $\nu_{\text{as}}(\text{POP})$, $\nu_{\text{s}}(\text{POP})$ and $\nu(\text{PO}_3)$ [12, 13, 20]. In the spectra of KErP_2O_7 (S2–S6) the range of the bands occurrence is the same as in the works [12, 13, 20], which confirms purity of the obtained products. Slight shifts of the POP bridges stretching vibration bands in the β -phase spectrum (S2, S3, and S5) in relation to that of the α -form (S4 and S6) are due to the structural differences between the hightemperature orthorhombic and the low-temperature monoclinic phase. A similar effect was observed and described in the works [13, 20].

Obtaining $\beta\text{-KErP}_2\text{O}_7$ in the samples S3 and S5 was quite surprising, since in view of the work [1] the transition from the monoclinic to the orthorhombic modification occurs in the temperature range 350–370 °C and at the applied synthesis conditions $\alpha\text{-KErP}_2\text{O}_7$ should be obtained. According to [1] discussed KErP_2O_7 diphosphate still has the highest temperature form with a hexagonal structure. Therefore, we found it necessary to conduct additional hightemperature XRD studies (DRON-2). The measurements were on the sample S2 (Table 1), which in the XRD studies carried out at room temperature had the β structure.

Figure 3a presents the XRD patterns of the sample S2 annealed for 1 h sequentially at the temperature 300, 350, 400, 750, 800 and 950 °C. Reflections characteristic of the monoclinic potassium erbium double diphosphate (KErP_2O_7) structure were observed at the temperature 300, 350 and 400 °C. Diffraction patterns of the sample annealed at 750 and 800 °C consisted of reflections indicating the presence of a mixture of the β and α modifications. At 950 °C, in addition to the α phase reflections, there were also reflections from erbium orthophosphate ErPO_4 . The obtained results indicated that short annealing time (1 h) in the temperature range 300–800 °C did not result in the formation of the pure phase α modification and

Table 1 Preparation of KErP₂O₇

Samples	Synthesis method	Starting reagents	Reagents molar ratio	Sintering parameters	Phases identified in the XRD patterns
S1	Ceramic method (in solid state)	ErPO ₄ , KPO ₃	1:1	500–900 °C, 1 day–2 weeks	ErPO ₄ and KPO ₃ , T > 800 °C–KErP ₂ O ₇ and ErPO ₄
S2	Ceramic method (in solid state)	Er ₂ O ₃ , KNO ₃ , (NH ₄) ₂ HPO ₄	1:2:4	250 °C, 2 weeks	Monoclinic KErP ₂ O ₇
S3	Ceramic method (in solid state)	Er ₂ O ₃ , KNO ₃ , (NH ₄) ₂ HPO ₄	1:2:4	500 °C, 48 h	Monoclinic KErP ₂ O ₇
S4	The ceramic method (in solid state)	Er ₂ O ₃ , KNO ₃ , (NH ₄) ₂ HPO ₄	1:2:4	500 °C, 48 h; then 750 °C, 3 days	Orthorhombic KErP ₂ O ₇
S5	The modified Pechini method [35]	Er ₂ O ₃ , KNO ₃ , NH ₄ H ₂ PO ₄	1:2:4	500 °C, 48 h	Monoclinic KErP ₂ O ₇
S6	The modified Pechini method [35]	Er ₂ O ₃ , KNO ₃ , NH ₄ H ₂ PO ₄	1:2:4	500 °C, 48 h; then 750 °C, 3 days	Orthorhombic KErP ₂ O ₇

Fig. 1 The XRD patterns of KErP₂O₇ at room temperature

annealing of KErP₂O₇ at 950 °C leads to its decomposition (reflections from ErPO₄). KErP₂O₇ is unstable at this temperature, so its hexagonal modification cannot exist.

Based on the discussed above XRD studies the maximum temperature of the high-temperature synthesis of α modification was determined. It is 750 °C (Table 1). In order to avoid any decomposition of KErP₂O₇ during prolonged heating the sintering temperature 750 °C was chosen. Also, based on the XRD studies the synthesis time was evaluated. Figure 3b shows the diffraction patterns of the sample S3 additionally annealed at 750 °C for 24, 48, and 72 h. It appeared that the transformation β to α modification occurs only after long annealing time (72 h). Also, by XRD analysis we examined the kinetics of the transformation from α to β modification. Figure 3c shows the diffraction patterns of the sample with the α structure

Fig. 2 FTIR spectra of KErP₂O₇

(sample S4) annealed at 250 °C for 1 and 2 weeks. We found that in both cases a mixture of the two KErP₂O₇ modifications (the monoclinic and orthorhombic) were present. In summary, the results of X-ray studies indicate that:

Fig. 3 **a** The high-temperature XRD patterns of sample S2. **b** The XRD patterns of the sample S3 annealed additionally at 750 °C in various times. **c** The XRD patterns of the sample S4 annealed at 250 °C in various times

- KErP_2O_7 phosphate occurs in two polymorphic forms: β -monoclinic and α -orthorhombic.
- KErP_2O_7 polymorphic transformation is enantiotropic but the transformation of one modification into another is very difficult. Due to the kinetic limitations and a slower diffusion of reagents in the solid phase and a significant difference in crystal structures of both modifications it requires the use of an appropriate heat treatment, hexagonal modification of KErP_2O_7 does not exist.

In order to determine the thermal characteristics of KErP_2O_7 phosphate, i.e. to establish its thermal stability, melting point (or decomposition temperature), and verification of the information on the existence of a high-temperature hexagonal polymorph DTA/DSC/TG thermal studies was carried out. The samples synthesized by different procedures shown in Table 1 were used in the studies. Figure 4 shows the DSC-heating curves of the samples S2–S6. On the DSC-heating curves of the S2, S3 and S5 samples only one endothermic effect with corresponding temperature 1025, 1012, 1006 °C, respectively, was observed. An analogous endothermic effect, but at slightly higher temperature, occurred on the DSC-heating curves of the samples S4 (1021 °C) and S6 (1029 °C). Another very weak endothermic effect was observed for these samples at approx. 358 °C. It can be attributed to β/α - KErP_2O_7 polymorphic transformation. The occurrence of this effect in the samples S4 and S6, and its absence in

Fig. 4 The DSC heating curves of KErP_2O_7

Fig. 5 The phase diagram of ErPO_4 – KPO_3 system. (Bullet symbols onset temperatures of endothermic effects appeared on DTA/DSC curves, times symbols melting temperatures of samples read by an optical pyrometer)

the samples S2, S3 and S5 confirms the results of the mentioned above XRD studies.

Due to the complicated conditions of the pure phase KErP_2O_7 phosphate synthesis, to establish phase equilibria and to construct the ErPO_4 – KPO_3 phase diagram two series of samples obtained from:

- ErPO_4 and KErP_2O_7 various mole ratio mixtures (sample S4—the orthorhombic modification), to determine the phase equilibria in the composition range 0–31.05 mass% KPO_3 .
- KErP_2O_7 (sample S4—the orthorhombic modification) and KPO_3 various mole ratio mixtures, to determine the phase equilibria in the rest of this system, i.e. richer in KPO_3 (>31.05 mass% KPO_3), were examined.

The prepared mixtures were sintered at 750 °C for 24 h (platinum crucibles). The resulting sinters were slowly cooled down to room temperature, then crushed and ground thoroughly. Their phase composition was monitored by X-ray diffraction analysis.

Figure 5 shows the proposed phase diagram of the ErPO_4 – KPO_3 system developed on the basis of the results of thermal studies. The endothermic effects seen on the DSC-heating curves of the samples at approx. 1025 °C (in the composition range from 26.4 to 75 mass% KPO_3) are assigned to peritectic KErP_2O_7 decomposition that occurs

Fig. 6 DTA/TG curves of heating of two selected samples from the ErPO_4 – KPO_3 system

according to the reaction $\text{KErP}_2\text{O}_7(\text{s}) \rightarrow \text{ErPO}_4(\text{s}) + \text{L}$. The β/α - KErP_2O_7 polymorphic transformation is reflected on the DSC-heating curves as a very weak effect at approx. 358 °C. They are only found in the samples with compositions included in the concentration range 21.7–72.4 mass% KPO_3 . Figure 6 shows the DTA/TG-heating curves of two selected samples from the composition range. According to Fig. 6 the mass loss observed on the TG curve starts at app. 1120 °C, so above the temperature of incongruent decomposition of KErP_2O_7 .

In the ErPO_4 – KPO_3 system the eutectic of composition: 92 mass% KPO_3 , 18 mass% ErPO_4 , exists, the melting point of which is 798 °C.

Potassium metaphosphate KPO_3 undergoes two polymorphic transformations: α/β at 449 °C and β/γ at 665 °C [29]. They were reflected on the DSC curves of the samples as thermal effects in the composition range 41.4–100 mass% KPO_3 . According to [33], KPO_3 metaphosphate decomposes at 1160 °C, so at the temperature considerably higher than the melting point. The mass loss accompanying the process does not affect the results of the studies on the phase equilibria in the ErPO_4 – KPO_3 system.

Conclusions

The phase diagram of the ErPO_4 – KPO_3 system was constructed on the basis of the comprehensive experimental investigations. One intermediate compound with the

formula KErP_2O_7 occurs in this system. It decomposes peritectically at about 1025 °C and exists in two polymorphic forms: monoclinic and orthorhombic.

Acknowledgements We would like to thank Witold Mielcarek from Electrotechnical Institute, Wrocław (Poland) for the high-temperature XRD experiment and its analysis.

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