

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

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Abstract The phase equilibria occurring in the $\text{ErPO}_4\text{--K}_3\text{PO}_4$ system were investigated by the thermal analysis, FTIR, and X-ray powder diffraction methods. On the basis of obtained results, the related phase diagram is proposed. This system includes one intermediate compound, $\text{K}_3\text{Er}(\text{PO}_4)_2$; the double phosphate melts incongruently at 1355 °C and occurs in two polymorphic forms; transformation $\beta/\alpha\text{-K}_3\text{Er}(\text{PO}_4)_2$ proceeds at 420 °C. The eutectic occurs at the composition of 58.5 wt% K_3PO_4 , 41.5 wt% ErPO_4 at 1317 °C.

Keywords Phase diagram · Potassium and erbium phosphates · DTA/DSC/TG/DTG · X-ray · FTIR

Introduction

Many papers about double phosphates of the general formula $\text{M}_3^{\text{I}}\text{Ln}(\text{PO}_4)_2$ (where M^{I} denotes an alkali metal and Ln is a rare earth element or Y or Sc) have been published. The information is mainly focused on the preparation methods, crystalline structure, and application possibilities of those compounds. According to the data, lanthanide-alkali metal double phosphates are of technological importance for applications in optics and electronics [1–10].

In view of relevant information from the literature, double phosphates of the formula $\text{M}_3^{\text{I}}\text{Ln}(\text{PO}_4)_2$ should occur in the systems of $\text{LnPO}_4\text{--M}_3^{\text{I}}\text{PO}_4$ (where Ln denotes a rare earth element or yttrium, and M^{I} does an alkali metal). According

to our research group results, such compounds occur in the $\text{Ln}_2\text{O}_3\text{--M}_3^{\text{I}}\text{O--P}_2\text{O}_5$ oxide systems on the $\text{LnPO}_4\text{--M}_3^{\text{I}}\text{PO}_4$ subsystems, where Ln = La, Ce, Nd, Y and M^{I} = Na, K, Rb [11–18]. It should be noted that, in the system $\text{YPO}_4\text{--Na}_3\text{PO}_4$, two intermediate compounds of $\text{Na}_3\text{Y}(\text{PO}_4)_2$ and $\text{Na}_3\text{Y}_2(\text{PO}_4)_3$ occur; both compounds melt congruently. Also, in the system $\text{YPO}_4\text{--Rb}_3\text{PO}_4$, two intermediate compounds occur; namely $\text{Rb}_3\text{Y}(\text{PO}_4)_2$ which melts congruently, and the $\text{Rb}_3\text{Y}_2(\text{PO}_4)_3$ which is unstable and decomposes in the temperature range between 1300 and 1330 °C. In each of the other investigated systems, a single intermediate of $\text{M}_3^{\text{I}}\text{Ln}(\text{PO}_4)_2$ occurs; it melts incongruently. Double phosphates $\text{M}_3^{\text{I}}\text{Ln}(\text{PO}_4)_2$ are usually obtained in a solid-state reactions by sintering an equimolar mixture of $\text{M}_3^{\text{I}}\text{PO}_4$ and LnPO_4 .

In the present paper, the results of investigation of the $\text{ErPO}_4\text{--K}_3\text{PO}_4$ subsystem are presented. The related phase diagram has not been reported so far. It is known from the literature that $\text{K}_3\text{Er}(\text{PO}_4)_2$ exists as well. According to Refs. [19, 20], the compound appears in two polymorphic modifications. The high-temperature one crystallizes in the hexagonal system (S.G. $P\bar{3}$, glaserite-type) and the low-temperature one does in the monoclinic system (S.G. $P2_1/m$, $a = 7.371(1)$, $b = 5.595(1)$, $c = 9.318(1)$ Å, and $\beta = 90.90(1)^\circ$). A polymorphic transition in $\text{K}_3\text{Er}(\text{PO}_4)_2$ exhibits at 436.4 °C [19].

The parent orthophosphates ErPO_4 and K_3PO_4 are known for congruent melting at 1896 ± 20 °C [21–23] and 1620 ± 20 °C [24], respectively. Polymorphism of both orthophosphates was investigated by many authors (see, e.g., [21, 24–31]). Erbium orthophosphate, ErPO_4 , is related to REPO_4 group with xenotime structure, isostructural to zircon (ZrSiO_4). Orthophosphate ErPO_4 crystallizes in the tetragonal system (S.G. $I41/amd$, $a = 6.8614(5)$, $c = 6.0082(9)$ Å, $Z = 4$) [21]. The compound exists in one

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polymorphic form. According to the literature on K_3PO_4 , polymorphism has revealed significant disagreements. This problem will be described in the “Results” section.

Experimental

The following commercial materials: Er_2O_3 (Aldrich), and $\text{NH}_4\text{H}_2\text{PO}_4$, $(\text{NH}_4)_2\text{HPO}_4$, K_2CO_3 , $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ (POCh)—all analytically pure were used to prepare the test samples from the ErPO_4 – K_3PO_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 [32]. Potassium orthophosphate K_3PO_4 was obtained from $\text{K}_3\text{PO}_4 \cdot 3\text{H}_2\text{O}$ by dehydration at 900 °C for 1 h.

Phase equilibria in the ErPO_4 – K_3PO_4 system were investigated by thermoanalytical methods and X-ray powder diffraction at room temperature.

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

The DSC/TG analysis during heating was carried out using a calorimeter SETSYSTM (TG–DSC 1500; SETARAM) 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 °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 (above 1400 °C) were 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 Na_3PO_4 (1583 °C) and $\text{Ca}_3(\text{PO}_4)_2$ (1810 °C). In the thermal analysis, the temperature read-out accuracy was ± 1.5 °C in a temperature range up to 800 and ± 3 °C above 800 and ± 30 °C when the temperature was read by the optical pyrometer.

The phase purity of the reagents and phase composition of the sinters and the melted samples for the investigated system were controlled by X-ray powder diffraction at room temperature. A SIEMENS D 5000 diffractometer

with CuK_α radiation ($\lambda = 0.154$ nm) were used. The measurements were performed in 2θ angle range of 10°–60°. The 2θ scanning speed was 0.02° s^{−1}. A Fourier transform infrared spectra was recorded on a PERKIN-ELMER SYSTEM 2000 FTIR spectrophotometer in the range of wavenumbers 400–1300 cm^{−1} using KBr pressed pellets.

Results

The phase diagram of the ErPO_4 – K_3PO_4 system, which was not known before, is shown in Fig. 1; it was elaborated in the entire composition range and temperatures ranging from room temperature to 1800 °C.

The experimental work was started with determining the most favorable conditions under which synthesis of the $\text{K}_3\text{Er}(\text{PO}_4)_2$ double phosphate would proceed to result in giving a phase-pure compound. The following were the starting materials: (1) Er_2O_3 , K_2CO_3 , and $(\text{NH}_4)_2\text{HPO}_4$ (mixed in the molar ratio of 1:3:4); (2) ErPO_4 , K_2CO_3 , and $(\text{NH}_4)_2\text{HPO}_4$ (mixed in the molar ratio of 2:3:2); (3) ErPO_4 and K_3PO_4 (mixed in the molar ratio of 1:1). After the mechanical processing (see “Experimental” section), the above compounds were sintered at different temperatures for different time intervals, which were followed by cooling to room temperature. Phase composition of each sinter

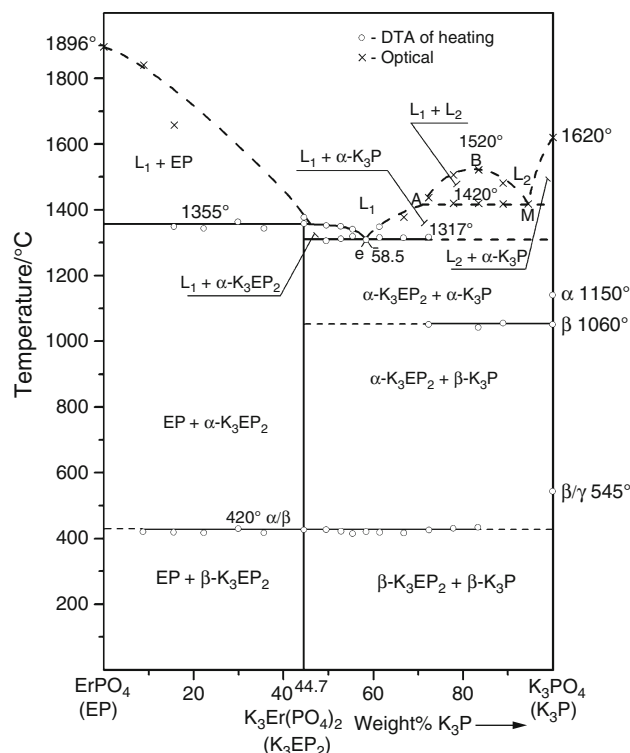


Fig. 1 The phase diagram of the ErPO_4 – K_3PO_4 system

was checked by X-ray powder diffraction. A synthesis procedure which consisted in sintering an equimolar mixture of ErPO_4 and K_3PO_4 at 1000 °C for 24 h was accepted as the most advantageous one. This procedure yielded a monoclinic modification of $\beta\text{-K}_3\text{Er}(\text{PO}_4)_2$. Attempts to obtain a high-temperature modification α by means of quenching-in-ice failed.

Next, the thermal characteristics of $\text{K}_3\text{Er}(\text{PO}_4)_2$ phosphate was investigated, including thermal stability, melting point, polymorphism. Three endothermic effects were found on the DTA-heating curve (Fig. 2a). Two successive effects, almost overlapping, occurred at high temperatures; the corresponding temperatures were 1355 ± 3 and 1365 ± 3 °C. DTA-heating examination of ErPO_4 -rich samples of the $\text{ErPO}_4\text{-K}_3\text{PO}_4$ system (Fig. 3a) was helpful to determine the phase transitions which the effects were related to (Fig. 1). The DTA curves of those samples showed an endothermic effect with corresponding temperatures between 1350 ± 3 and 1358 ± 3 °C. Based on this, it has been determined that:

- $\text{K}_3\text{Er}(\text{PO}_4)_2$ phosphate is unstable at high temperatures; it melts incongruently at 1355 ± 3 °C with the formation of solid ErPO_4 and a melt richer in K_3PO_4 ,

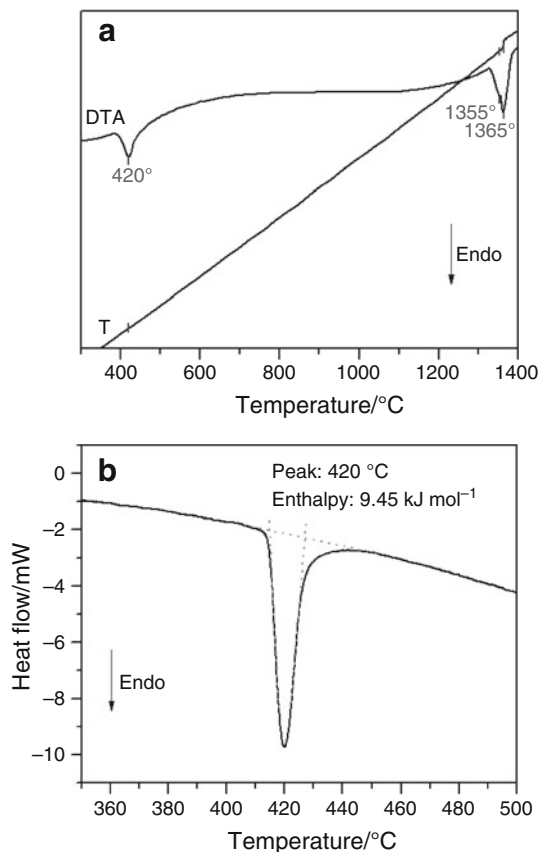


Fig. 2 Thermal analysis of heating of $\text{K}_3\text{Er}(\text{PO}_4)_2$: **a** T and DTA data, **b** DSC result

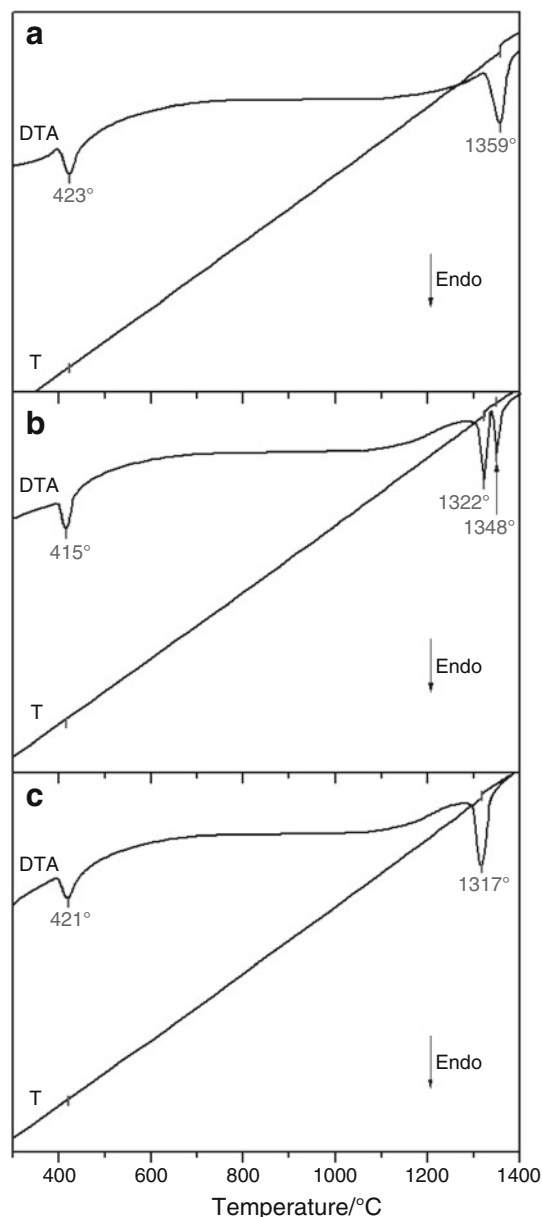


Fig. 3 T and DTA curves of the samples from the $\text{ErPO}_4\text{-K}_3\text{PO}_4$ system: **a** 30 wt% K_3PO_4 , 70 wt% ErPO_4 ; **b** 55 wt% K_3PO_4 , 45 wt% ErPO_4 ; **c** 58.5 wt% K_3PO_4 , 41.5 wt% ErPO_4

- the 1365 °C endothermic effect was connected with the liquidus curve.

A temperature of 420 ± 1.5 °C corresponded to the third endothermic effect shown by the DTA-heating curve of $\text{K}_3\text{Er}(\text{PO}_4)_2$ phosphate. This effect was ascribed to the $\beta/\alpha\text{-K}_3\text{Er}(\text{PO}_4)_2$ transformation. Enthalpy of the transformation, as determined on the basis of calorimetric analysis (DSC, Fig. 2b), amounts to 9.45 ± 1.89 kJ mol⁻¹. According to Ushakov et al. [19], the β/α transition occurs at a temperature of 436.4 °C, and the accompanying thermal effect is larger and amounts of 15.20 ± 3.99 kJ mol⁻¹.

The FTIR spectrum of obtained β - $\text{K}_3\text{Er}(\text{PO}_4)_2$ at 1000°C (Fig. 4) displays the characteristic bands of $\text{M}_3\text{Ln}(\text{PO}_4)_2$ orthophosphates [20]. The main absorption bands are observed at 407 – 413 , 540 – 620 , 938 , and 970 – 1120 cm^{-1} . The bands at 407 – 413 and 540 – 620 cm^{-1} are due to the symmetric ν_2 and asymmetric ν_4 deformation modes of the PO_4^{3-} group, respectively. The band at 938 cm^{-1} corresponds to the symmetric stretching ν_1 of PO_4^{3-} group and the intensive bands at 970 – 1120 cm^{-1} to the asymmetric stretching vibrations ν_3 of the P–O bands.

The following two series of samples for investigation were prepared due to the conditions under which the $\text{K}_3\text{Er}(\text{PO}_4)_2$ compound was formed and, too, the need to have the samples in the equilibrium state:

- unequimolar mixtures of ErPO_4 and $\text{K}_3\text{Er}(\text{PO}_4)_2$ in the ErPO_4 -rich part of the system (in the composition range of 0 – $44.7\text{ wt}\%$ K_3PO_4 ,
- unequimolar mixtures of $\text{K}_3\text{Er}(\text{PO}_4)_2$ and K_3PO_4 in the K_3PO_4 -rich part of the system (i.e., above $44.7\text{ wt}\%$ K_3PO_4).

After the initial mechanical processing (see “Experimental” section), the mixtures were pressed into pellets and solid state sintered at 1000°C for 24 h. Next, those were slowly cooled to room temperature and the sinters were crushed and thoroughly rubbed. Such preparations were then investigated by DTA of heating and X-ray diffraction.

Diffraction patterns of three representative samples of the ErPO_4 – K_3PO_4 system (30 , 44.7 , and $70\text{ wt}\%$ K_3PO_4) are shown in Fig. 5. Comparing the displayed reflections with the ones of the ICDD PDF database for ErPO_4 (card no. 1-72-336), for K_3PO_4 (card no. 20-0921), and $\text{K}_3\text{Er}(\text{PO}_4)_2$ (card no. 49-1019), indicates that only one intermediate compound is formed in the examined system, namely the $\text{K}_3\text{Er}(\text{PO}_4)_2$ binary orthophosphate. Reflections

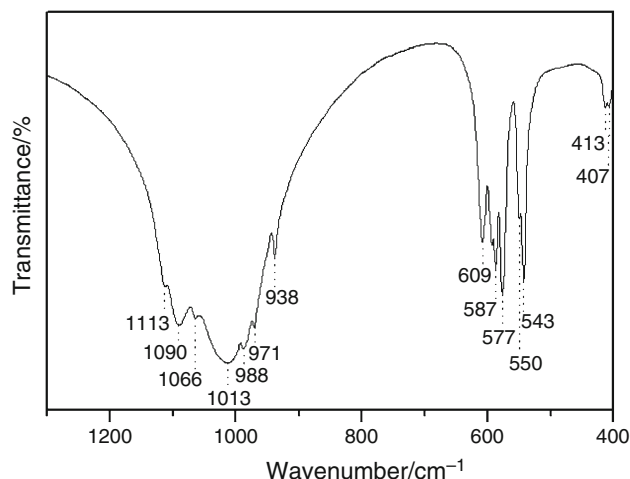


Fig. 4 FTIR spectrum of $\text{K}_3\text{Er}(\text{PO}_4)_2$

present on the diffraction pattern shown in Fig. 5a are typical of ErPO_4 and $\text{K}_3\text{Er}(\text{PO}_4)_2$, whereas those in Fig. 5c are characteristic of $\text{K}_3\text{Er}(\text{PO}_4)_2$ and K_3PO_4 phosphates. The diffraction pattern in Fig. 5b demonstrates features of the phase-pure intermediate $\text{K}_3\text{Er}(\text{PO}_4)_2$ which was self-synthesized; in addition, for comparison, bar graph is given (PDF card no. 49-1019).

Samples of the ErPO_4 – K_3PO_4 system were melting at high temperatures (mostly above 1400°C); hence, prepared sinters were melted in a horizontal furnace. Fusion temperature was read by pyrometer and thus the liquidus curves in Fig. 1, as drawn with mostly dashed lines, have a suggested shape only.

Also, based on the thermoanalytical investigations (distribution of melting point), it has been observed that within the composition range from about 70 to about $95\text{ wt}\%$ K_3PO_4 , an area of a limited solubility of the components occurs in the liquid phase below $1520 \pm 30^\circ\text{C}$. The liquid undergoes separation into two liquid solutions, L_1 and L_2 . An area of unlimited mutual solubility occurs above the temperature $1520 \pm 30^\circ\text{C}$, which is above point B. Composition of the solution L_1 changes along curve BA with decreasing temperature, while that of L_2 does along curve BM. The liquid L_2 reaches the composition corresponding to the point M (monotectic point) at a temperature of $1420 \pm 30^\circ\text{C}$. There starts a monotectic transition which proceeds at the constant temperature $1420 \pm 30^\circ\text{C}$ according to the reaction



where L_{2M} denotes the liquid L_2 of composition at point M, and L_{1M} does the liquid L_1 of composition at point A.

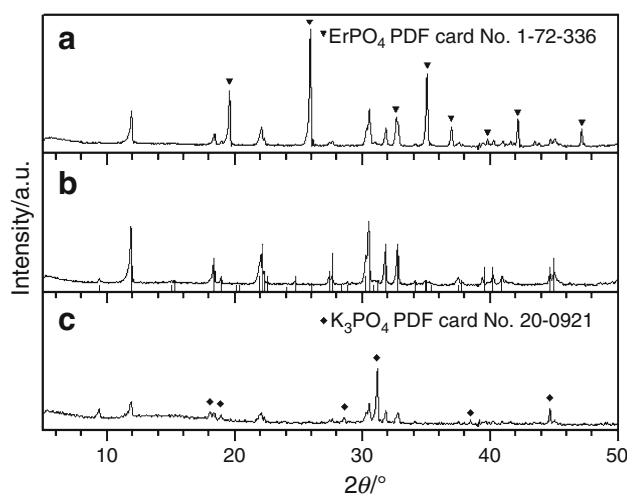


Fig. 5 XRD of the samples from the ErPO_4 – K_3PO_4 system: **a** $30\text{ wt}\%$ K_3PO_4 , $70\text{ wt}\%$ ErPO_4 ; **b** $\text{K}_3\text{Er}(\text{PO}_4)_2$ and, for comparison, bar graph is shown (PDF card no. 49-1019); **c** $70\text{ wt}\%$ K_3PO_4 , $30\text{ wt}\%$ ErPO_4

Also, the occurrence of a eutectic is found; it melts at a temperature of 1317 ± 3 °C (Fig. 3b, c). The eutectic point parameters are 58.5 wt% K₃PO₄, 41.5 wt% ErPO₄. Effects connected with the eutectic transformation occur on the DTA-heating curves of samples with the composition range from 45 to about 72 wt% K₃PO₄ (Figs. 1, 3b, c). Samples with a higher content of potassium orthophosphate do not exhibit those effects. As was mentioned, the K₃Er(PO₄)₂ phosphate melts incongruently at 1355 ± 3 °C. Endothermic effects accompanying this temperature are present on the DTA-heating curves for ErPO₄-rich samples up to 46 wt% K₃PO₄. Peritectic reaction ends at the latter composition (Fig. 1). Endothermic effects at about 420 ± 1.5 °C, which are connected with the β/α -K₃Er(PO₄)₂ transformation, are observed on the DTA-heating curves for all samples of the composition range from 10 to 85 wt% K₃PO₄.

Polymorphism of K₃PO₄ was reexamined earlier (1981 year) in our laboratory by the thermal, dilatometric, and X-ray methods [24]. The sintered and the molten potassium orthophosphate was investigated during heating and cooling. It was discovered that the compound appeared in three polymorphic modifications. The transitions in molten K₃PO₄ during heating took place at 545 °C (γ/β) and 1060–1150 °C (β/α). Over the temperature range between 1060 and 1150 °C, a mixture of α and β modifications occurred [24]. In the ErPO₄–K₃PO₄ system under discussion, the β/α -K₃PO₄ transition proceeds only at a temperature of 1060 ± 3 °C. A single endothermic effect is observed on the DTA-heating curves of the melted samples; moreover, it is found for the potassium orthophosphate-rich samples, i.e., the ones containing from 70 to 100 wt% K₃PO₄. Any heating effects, however, have not been observed, which could be connected with the γ/β -K₃PO₄ transformation.

Conclusions

The phase diagram of the K₃PO₄–ErPO₄ system was determined in the temperature range 20–1896 °C. In the system one, intermediate compound K₃Er(PO₄)₂ was found. It occurs in two polymorphic forms; transformation β/α -K₃Er(PO₄)₂ proceeds at 420 °C. K₃Er(PO₄)₂ phosphate is unstable at high temperatures and melts incongruently at 1355 °C. The minimum melting temperature is 1317 °C and it corresponds to the binary eutectic K₃PO₄ + ErPO₄ with composition of 58.5 wt% K₃PO₄, 41.5 wt% ErPO₄.

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