The revised phase diagram of the $\text{Ca}_3(\text{PO}_4)_2$ – YPO_4 system. The temperature and concentration range of solid-solution phase fields

Aleksandra Matraszek · Ewa Radomińska

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Abstract A revised version of the $\text{Ca}_3(\text{PO}_4)_2$ – YPO_4 phase diagram has been proposed on the basis of results obtained by thermal analysis (DTA/DSC/TG) and X-ray diffraction methods. A limited solid solution with the structure of $\beta\text{-Ca}_3(\text{PO}_4)_2$ exists in the system. At 1,100 °C the maximal concentration of YPO_4 in the solid solution is ~15 mass%. The solid-solution phase field exists in the temperature range upto ~1,380 °C. Two high-temperature solid solutions with the structure of α' and $\alpha\text{-Ca}_3(\text{PO}_4)_2$ form in system as well, however only the α phase can be obtained by quenching from high temperatures. The $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ compound with the structure of eulytite forms in the $\text{Ca}_3(\text{PO}_4)_2$ – YPO_4 system at temperatures exceeding 1,255 °C and does not show any polymorphic transition.

Keywords Calcium phosphate · Rare earth compounds · Phase diagram · Thermal analysis · X-ray diffraction

Introduction

Calcium phosphates have aroused much interest as bioactive compounds. They are used as components of different kinds of materials applied in dental and orthopedic surgery [1, 2].

Among other bioactive calcium compounds, tricalcium bis(phosphate), $\text{Ca}_3(\text{PO}_4)_2$, is one of the most interesting materials. It melts congruently at a high temperature ($T_m = 1,810$ °C) [3], and it has three polymorphic modifications: β , α , and α' . The α' form exists at temperatures above 1430 °C [4] and it has a trigonal structure (S.G $\text{P}\bar{3}\text{m}$) with parameters: $a = b = 5.3507(8)$, $c = 7.684(1)$ Å [5]. It is not possible to overcool the polymorph, even in the course of quenching.

The $\alpha\text{-Ca}_3(\text{PO}_4)_2$ form is stable in a temperature range of 1,125–1,430 °C [6–8] and has a monoclinic structure with a $\text{P}2_1/\text{a}$ space group [5, 9]. The biodegradation and bioreabsorption processes of $\alpha\text{-Ca}_3(\text{PO}_4)_2$ occur in physiological environment faster than that of hydroxyapatite and $\beta\text{-Ca}_3(\text{PO}_4)_2$. This makes the α -phase suitable for application as osteoconductive material and/or biodegradable drug carrier [10, 11].

At temperatures below 1,125 °C exists the low-temperature $\beta\text{-Ca}_3(\text{PO}_4)_2$ form, which is characterized by a trigonal structure with unit cell parameters: $a = b = 10.4352(2)$ Å, $c = 37.4029(5)$ Å [12]. The structure of the phase is complicated: there are five cationic sites with coordination number relative to oxygen from 3 to 8. In pure $\beta\text{-Ca}_3(\text{PO}_4)_2$ or doped with divalent cations one of the Ca sites is half occupied [13, 14]. The same Ca position is empty for RE^{3+} doping, which is associated with charge balance mechanism [15, 16]. This feature of the structure makes the $\beta\text{-Ca}_3(\text{PO}_4)_2$ phase a perfect host lattice for doping with mono-, di-, and/or trivalent cations. The wide range of dopants and doping concentrations enables modification of physicochemical properties of $\text{Ca}_3(\text{PO}_4)_2$. The $\beta\text{-Ca}_3(\text{PO}_4)_2$ -derived phases show optical activity [17–20], are considered as bioceramics or biocements [21–26] and show interesting electric properties [27–29].

The $\beta \rightarrow \alpha$ structural change has a reconstructive character. This implies that a long-term heating at a

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A. Matraszek (✉) · E. Radomińska
Department of Inorganic Chemistry, Faculty of Engineering and Economics, Wrocław University of Economics, Komandorska 118/120, 53-345 Wrocław, Poland
e-mail: aleksandra.matraszek@ue.wroc.pl

temperature above the phase transition point is necessary to complete the $\beta \rightarrow \alpha$ transformation. The process is reversible, however due to the high activation energy of the $\alpha \rightarrow \beta$ transformation the monoclinic form of $\text{Ca}_3(\text{PO}_4)_2$ does not revert to the low-temperature form, when cooled with moderate cooling rate ($5\text{ }^\circ\text{C min}^{-1}$) [8, 30].

The thermodynamically stable form of YPO_4 is of xenotime type with structural parameters of tetragonal elementary cell (S.G. I41/amd): $a = 6.8840(3)$, $c = 6.0202(3)\text{ }\text{\AA}$ [31]. It is refractory material with a melting point at $1,995 \pm 20\text{ }^\circ\text{C}$ [32] or $2,150\text{ }^\circ\text{C}$ [33].

Phase diagrams of phosphate systems with rare earth elements have been studied by our group in last decades [34–39]. In the $\text{Ca}_3(\text{PO}_4)_2$ - REPO_4 systems ($\text{RE} = \text{Y}, \text{La}, \text{Ce}$) form compounds with the formula $\text{Ca}_3\text{RE}(\text{PO}_4)_3$ [34–36]. They exist only at high temperatures and have a regular structure of eulytite (S.G. I43d) [40, 41]. It has been also reported that the $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ phase has a complicated thermal behavior. According to Ref. [34] the phosphate melts congruently at $1,790\text{ }^\circ\text{C}$ and at temperatures below $1,215\text{ }^\circ\text{C}$ it decomposes to YPO_4 and $\text{Ca}_3(\text{PO}_4)_2$. In addition, the compound has a reversible $\beta \rightarrow \alpha$ polymorphic transition at $1,255\text{ }^\circ\text{C}$. The $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ phase forms with $\text{Ca}_3(\text{PO}_4)_2$ and YPO_4 two eutectic systems with melting temperature at $1,684$ and $1,674\text{ }^\circ\text{C}$, respectively. The $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ phase can be quenched to room temperature, however, during heating/cooling with rate of $40\text{--}400\text{ }^\circ\text{C min}^{-1}$ occurs a martensitic transformation [41].

In the $\text{Ca}_3(\text{PO}_4)_2$ - REPO_4 systems ($\text{RE} = \text{La}, \text{Ce}, \text{and Eu}$) fields of limited solid solution with the structure of β - $\text{Ca}_3(\text{PO}_4)_2$ were found [16, 35, 36]. In contrast to the results, the study of the phase relationships in the $\text{Ca}_3(\text{PO}_4)_2$ - YPO_4 system did not consider existence of any type of solid solution [34]. The comparison of the most recent phase equilibria studies of systems with $\text{Ca}_3(\text{PO}_4)_2$ implies that the phase relationships in the $\text{Ca}_3(\text{PO}_4)_2$ - YPO_4 system are more complicated as presented in the Ref. [34]. Because of an growing interest on materials derived from $\text{Ca}_3(\text{PO}_4)_2$ and doped with rare earth elements, a revision of the $\text{Ca}_3(\text{PO}_4)_2$ - YPO_4 system has been undertaken. The aim of the present research was to clarify the divergences between reported studies with the attention focused on thermal and concentration range of solid-solution phase fields, as well as on the polymorphism of the $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ eulytite phase.

Experimental

Synthesis

The following analytical reagents were used to obtain the $\text{Ca}_3(\text{PO}_4)_2$ compound: CaCO_3 , CaHPO_4 (analytical grade,

POCH Gliwice). The phosphate was prepared in a solid state by the ceramic method according to method proposed in [42]. In this synthesis route, a stoichiometric mixture of CaCO_3 and $\text{Ca}_2\text{P}_2\text{O}_7$ was annealed at $900\text{ }^\circ\text{C}$ for 5 h, which was followed by grinding in an agate mortar and heating for 5 h at $1,400\text{ }^\circ\text{C}$. The $\text{Ca}_2\text{P}_2\text{O}_7$ compound was prepared from CaHPO_4 by calcination at $900\text{ }^\circ\text{C}$ (2 h).

The YPO_4 was obtained by precipitation from a suspension of Y_2O_3 (99.99 %, POCh, Poland) in diluted H_3PO_4 (85 %, POCh Gliwice). The molar ratio of $[\text{PO}_4^{3-}]:[\text{Y}^{3+}]:\text{H}_2\text{O}$ was 1:0.023:25. The suspension was boiled under reflux for at least 6 h. The obtained precipitate was filtered and washed with hot distilled water. Finally, the powder was calcined at $1,400\text{ }^\circ\text{C}$ for 2 h to expel moisture and adsorbed pyrophosphates.

The binary samples of the $\{(100-x)\text{Ca}_3(\text{PO}_4)_2 + x\text{-YPO}_4\}$ composition, where $x \leq 50$ (x —the mass% of YPO_4), were synthesized by carefully grinding of a mixture of $\text{Ca}_3(\text{PO}_4)_2$ and YPO_4 . The chemical composition of samples under study is shown in the Tab. S1 (supplementary material). The powders were pelletized, preliminary heated at $900\text{ }^\circ\text{C}$ for 10 h, and finally at $1,100\text{ }^\circ\text{C}$ for 40 h in several heating steps. Between the stages samples were quenched, ground, and homogenized in an vibratory mill (Fritsch, Pulverisette 23) in isopropanol. The phase composition of samples was examined by X-ray diffraction (XRD) method. The same results of XRD measurements after two annealing steps were a prove that equilibrium state had been reached.

The $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ eulytite was obtained from $\text{Ca}_2\text{P}_2\text{O}_7$ and Y_2O_3 . The ground and pelletized mixture of the reagents was quenched after sintering stage at $1,400\text{ }^\circ\text{C}$ for 10 h.

The samples were quenched from high temperatures (above $1,400\text{ }^\circ\text{C}$) as follows: the pelletized powders were closed in welded ampoules made of Pt30Rh and after appropriate heating steps dropped into a mixture of water and ice from a vertical tubular furnace.

Characterization methods

The DTA/TG experiments were carried out using Derivatograph 3427 (MOM, Hungary). The samples were heated in a temperature range of $20\text{--}1,450\text{ }^\circ\text{C}$ (heating rate: $7.5\text{ }^\circ\text{C min}^{-1}$, Pt crucible, sample mass $450\text{--}600\text{ mg}$, air atmosphere). The temperature calibration factor for the thermal experiments was obtained at the phase transition temperature of K_2SO_4 ($583\text{ }^\circ\text{C}$), its melting point ($1,070\text{ }^\circ\text{C}$) and the melting point of $\text{Ca}_2\text{P}_2\text{O}_7$ ($1,353\text{ }^\circ\text{C}$).

Phase analysis of the samples was made using XRD technique and a Siemens D5000 diffractometer equipped with a Cu X-ray tube. The measurements were performed in 2θ range of $5\text{--}80^\circ$ with a 0.02° step and at least 4 s per

Fig. 1 The XRD patterns of samples with different YPO_4 concentration. Samples were obtained by quenching from 1,100 °C

step. Silicon (99.995 % ABCR GmbH) was used as an external standard for refinement of structural parameters. Lattice constants of the $\beta\text{-Ca}_3(\text{PO}_4)_2$ unit cell were refined using Checkcell software [43].

Results and discussion

Phase equilibria study

The phase composition of samples sintered at selected temperatures was obtained by the XRD measurements. In the diffraction patterns of samples sintered at 1,100 °C the main phase was $\beta\text{-Ca}_3(\text{PO}_4)_2$ (Fig. 1). The YPO_4 phase was found in samples with $x(\text{YPO}_4) \geq 20$ mass%. It should be also mentioned that several of the most intensive YPO_4 reflections overlapped with these of $\beta\text{-Ca}_3(\text{PO}_4)_2$. This made the qualitative analysis of the patterns complicated. The SEM study of the samples confirmed that the samples with $x > 25$ mass% are biphasic. In the Fig. 2 are shown the BSE images of samples with $x(\text{YPO}_4) = 15$ –30 mass%. The sample with the lowest content of YPO_4 has a single-phase character (Fig. 2a). In the images of samples with $x = 25$ and 30 mass% secondary grains of light color are visible (Fig. 2b, c). The

light color of grains is connected with high concentration of yttrium (element with high mass number). Unfortunately, the yttrium L line (1.922 keV) is very close to the P(K) absorption edge (2.013 keV). Since the lines overlap, the accurate determination of Y concentration in samples containing both elements (yttrium and phosphorus) can be not determined.

The lattice constants of the $\beta\text{-Ca}_3(\text{PO}_4)_2$ unit cell for samples with the $x \leq 25$ mass% were refined using the Checkcell software on basis of the $\beta\text{-Ca}_3(\text{PO}_4)_2$ phase parameters reported in [13]. The change of the obtained lattice constants versus molar fraction of YPO_4 is shown in Fig. 3 and the values are shown in Table 1. There is an evident decrease of c parameter value in the concentration range of 0–15 mass% (0–23 mol%) and according to the Vegard's rule in the range exists the limited solid solution of YPO_4 in $\beta\text{-Ca}_3(\text{PO}_4)_2$. The ionic radius of yttrium (1.02 Å) is smaller than that of calcium 1.12 Å [44] and hence the exchange of yttrium for calcium ions in the structure of $\beta\text{-Ca}_3(\text{PO}_4)_2$ results in a decrease of the solid solution unit cell volume (Table 1).

The chemical composition of the obtained solid solution can be expressed by the formula: $\text{Ca}_{3-3z}\text{Y}_z(\text{PO}_4)_2$, where z is the molar fraction of YPO_4 . Yttrium is introduced into the structure of $\beta\text{-Ca}_3(\text{PO}_4)_2$ with simultaneous formation of vacancy according to the scheme: $3\text{Ca}^{2+} \rightarrow 2\text{Y}^{3+} + \square$ [15, 16]. It has been stated in Refs. 15–17 that the maximal REPO_4 concentration in the $\beta\text{-Ca}_3(\text{PO}_4)_2$ solid solution should not exceed 25 mol%. The maximal RE concentration is connected with the fact that at that point, the smallest and irregular Ca site is completely vacant [16, 17].

The phase composition of samples quenched from 1,400 °C was depended on mass content of YPO_4 . The Fig. 4 presents the XRD patterns of samples with $x \leq 12$ mass% of YPO_4 heated at the temperature.

In the sample with 2.4 mass% of YPO_4 reflections of only $\alpha\text{-Ca}_3(\text{PO}_4)_2$ have been found. The same phase composition has been found by XRD for the sample quenched from 1,600 °C. The pellets quenched from high temperatures were cracked, which was a sign of transitions occurring in the material. In order to obtain the sample with $x(\text{YPO}_4) = 2.4$ mass% in the α structure, quenching from high temperatures was necessary. The same powders cooled in an electric furnace with moderate cooling rate were characterized by the presence of only β phase. This finding is in contradiction with the metastable character of the overcooled α form in the $\text{Ca}_3(\text{PO}_4)_2$ – $\text{Mg}_3(\text{PO}_4)_2$ system [8]. The authors of the manuscript stated that quenching is not required to retain the α phase on cooling.

The preparation with $x = 5$ mass% of YPO_4 was diphasic; both α and $\beta\text{-Ca}_3(\text{PO}_4)_2$ phase reflections were identified in the XRD pattern (Fig. 4). The diffractogram of

Fig. 2 The SEM images (the BSE mode) of samples quenched from 1,100 °C. Sample with $x(\text{YPO}_4) = 15$ (a), 25 (b), and 30 mass% (c)

Fig. 3 The unit cell parameters of the solid solution of YPO_4 in $\beta\text{-Ca}_3(\text{PO}_4)_2$ versus molar fraction of YPO_4

the sample quenched from 1,600 °C did not show considerable changes. On the DTA curve of the powder, three endothermic effects were registered at 1305, 1375, and 1420 °C.

The powders with $10 < x < 50$ sintered at 1,400 °C were biphasic and contained $\beta\text{-Ca}_3(\text{PO}_4)_2$ solid solution and $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ phosphate.

The presence of the β phase in the samples quenched from high temperatures was surprising, since the α/α' -

Table 1 The lattice parameters of $\text{Ca}_{3-3x}\text{Y}_x(\text{PO}_4)_2$ solid solution in samples heated at 1,100 °C for 40 h and quenched in ice

Molar fraction of YPO_4/z	$a/\text{\AA}$	$c/\text{\AA}$	$V/\text{\AA}^3$
0.0398	10.436(5)	37.373(5)	3524.8(8)
0.0815	10.432(4)	37.361(10)	3521.3(8)
0.1578	10.430(3)	37.345(10)	3518.3(9)
0.2294	10.432(3)	37.325(5)	3517.9(9)
0.2966	10.430(2)	37.335(5)	3517.3(10)
0.3599	10.431(3)	37.326(15)	3517.3(8)

$\text{Ca}_3(\text{PO}_4)_2$ solid solutions formation has been evidenced in the sample with the lowest YPO_4 content. As mentioned above, on the DTA curves of the powders with the low YPO_4 content, thermal effects connected to phase transitions have been observed. The presence of the β form instead of the α (or α') solid solution could be explained by the probable lower energy barrier of the $\alpha \rightarrow \beta$ transition occurring on cooling in the $\text{Ca}_3(\text{PO}_4)_2$ solid solutions in comparison to the undoped $\text{Ca}_3(\text{PO}_4)_2$. Since the high-energy barrier stabilizes the metastable α phase at room temperature, its lowering should result in rapid transition and presence of the low-temperature solid solution in samples quenched from high temperatures. At the same

Fig. 4 The XRD patterns of samples with different YPO_4 concentration quenched from 1,400 °C

time, the α' modification of $\text{Ca}_3(\text{PO}_4)_2$ could be not obtained by quenching [4].

Thermal behavior of $\text{Ca}_3\text{Y}(\text{PO}_4)_3$

The $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ phosphate belongs to phases existing at high temperatures. Presence of the compound was identified only in samples quenched from temperatures above 1,255 °C. In the present study, the phase pure compound has been obtained by reacting of $\text{Ca}_2\text{P}_2\text{O}_7$ and Y_2O_3 at 1,400 °C. In the previously published studies [35, 36, 45] it has been shown that the most effective route to obtain phase pure $\text{Me}_3\text{RE}(\text{PO}_4)_3$ phases is the application of more reactive substrates, for instance $\text{Me}_2\text{P}_2\text{O}_7$ and RE oxides. This eliminates the problem with the relative slow eulytite formation, which is dependent on diffusion processes occurring upon $\beta\text{-Ca}_3(\text{PO}_4)_2$ solid solution decomposition. In addition, quenching from high temperatures (above of $\sim 1,250$ °C) is necessary to obtain single-phase powders. When quenched, the $\text{Me}_3\text{RE}(\text{PO}_4)_3$ phases show metastable character, since slow diffusion in bulk at room temperature stops the decomposition of the compound.

The thermal behavior of phase pure $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ was studied by DTA (Fig. 5a) and XRD (Fig. 6) techniques. On the heating curve of the compound quenched from 1,400 °C two thermal effects were identified: exothermic

Fig. 5 The DTA curves of heating of $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ compound obtained by quenching from 1,400 °C (a) and the same sample subjected to heating 20 h at 1,100 °C (b)

Fig. 6 The XRD patterns of $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ compound obtained at 1,400 °C (a) and the same sample after heating at 400 °C (b), 1,240 °C (c), and 1,285 °C (d)

Fig. 7 The phase diagram of the $\text{Ca}_3(\text{PO}_4)_2$ – YPO_4 system. The abbreviations α'_{ss} , α_{ss} , and β_{ss} denote, respectively, α' , α , and β - $\text{Ca}_3(\text{PO}_4)_2$ solid solutions. [∇ —onset temperatures of endothermic effects registered on DTA heating curves]

and endothermic one at, respectively, 840 and 1,275 °C (Fig. 5a).

The single-phase powder (consisting of eulytite phase only) subjected to 20 h heating at 1,100 °C was biphasic (Fig. 6c). It composed of a mixture of β - $\text{Ca}_3(\text{PO}_4)_2$ solid solution and YPO_4 and showed a slightly different thermal behavior (Fig. 5b). No exothermic effects were observed on the DTA curve, however, two endothermic effects were recognized: one broad and weak peak at $\sim 1,255$ °C and one strong effect at 1,315 °C.

The XRD patterns of the $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ sample heat treated at different temperatures (Fig. 6) helped to explain the observed thermal effects. The $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ compound has been found in powders quenched from 1,400 and 1,285 °C (Fig. 6a, d). Heating of the phase pure phosphate at a temperature below 840 °C, i.e., below the temperature of the exothermic effect, did not change the phase composition of the powder, it remained single phase (Fig. 5b). The same powder quenched from 1,100 and 1,240 °C was biphasic and composed of a mixture of YPO_4 and β - $\text{Ca}_3(\text{PO}_4)_2$ solid solution (Fig. 6c). From the results of the XRD study, it can be concluded that the formation point of $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ lies between 1,240 and 1,285 °C and the metastable phase decomposes at temperature range 840–1,255 °C.

Summarizing, the thermal effects visible on the DTA heating curves of $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ (Fig. 5) can be attributed to following processes:

- decomposition of the overcooled (metastable) $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ phase into the β - $\text{Ca}_3(\text{PO}_4)_2$ solid solution and YPO_4 at ~ 840 °C (the exothermic effect in Fig. 5a);

- crystallization of the $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ phase from parent phosphates taking place in a temperature range (the endothermic effects on both DSC curves in the temperature range 1,255–1,315 °C).

The onset temperature of the first endothermic effect (1,255 °C) was chosen as the starting point of the compound synthesis from YPO_4 and β - $\text{Ca}_3(\text{PO}_4)_2$ solid solution. The formation of $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ occurs with difficulties at this temperature because it is accompanied by a significant change in the chemical composition of the solid solution being in equilibrium. Above 1,255 °C the $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ compound should be regarded as a thermodynamically stable phase.

The observed thermal behavior of the $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ compound is similar to that of the $\text{Ca}_3\text{Ce}(\text{PO}_4)_3$ and $\text{Sr}_3\text{Ce}(\text{PO}_4)_3$ phases [36, 45]. The phases can be quenched from temperatures exceeding their formation point and they are metastable present at room temperature. Upon heating of the metastable phases at a moderate temperature (upto ~ 800 °C) the decomposition of the phosphates is stopped, by kinetic hindrances. First at ~ 800 °C starts the decomposition, which manifests on DTA curves in form of exothermal effects. Above the temperature, the powders can attain the equilibrium state. Under further heating YPO_4 and β - $\text{Ca}_3(\text{PO}_4)_2$ solid solution react at a temperature above of 1,255 °C, which results in formation of the eulytite-type phase. The synthesis of the high-temperature phosphate is accompanied by a registration one or two endothermic effects on the DTA heating curves. The same thermal behavior has been registered for the $\text{Ca}_3\text{Ce}(\text{PO}_4)_3$ phase [36].

It has been shown in [34] that the $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ phosphate forms at 1,215 °C and has a polymorphic transition at 1,255 °C. In contrast to the statement, it has been above revealed that the compound is not a stable phase at 1,240 °C. In addition, in Refs. [38, 45] it has been shown that the thermal effects connected to the formation/decomposition of $\text{Me}_3\text{RE}(\text{PO}_4)_3$ are characterized by a large thermal hysteresis. The difference between the onset temperatures of effects on heating and cooling DTA curves is connected to kinetic hindrances occurring by the decomposition/formation of new phases and is a sign of reconstructive-type transformations [45, 46]. Because the experiments presented in [34] were carried out in cooling runs, the most probably the effects at 1,215 and 1,255 °C were both connected to the decomposition of $\text{Ca}_3\text{Y}(\text{PO}_4)_3$.

The phase diagram of the $\text{Ca}_3(\text{PO}_4)_2$ – YPO_4 system

On basis of results of the XRD and DTA study, it was possible to propose a revised version of the $\text{Ca}_3(\text{PO}_4)_2$ – YPO_4 phase diagram (Fig. 7). The figure summarizes all onset temperatures of the endothermic effects registered during the DTA heating runs of samples sintered at 1,100 °C. The temperature and composition of eutectic points, as well as the melting point of $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ have been adopted from [34]. The melting point of $\text{Ca}_3(\text{PO}_4)_2$ has been taken from [3].

There are three solid-solution phase fields. The composition range of the limited solid solution of YPO_4 in β - $\text{Ca}_3(\text{PO}_4)_2$ has been found by the XRD study. At 1,100 °C the maximal content of YPO_4 in the solid solution is ~15 mass% (~23 mol%).

The existence of the limited solid solutions at high temperatures has been evidenced by the observed temperature change of $\beta \rightarrow \alpha$ and $\alpha \rightarrow \alpha'$ transitions. The limited solid solutions with the α and α' - $\text{Ca}_3(\text{PO}_4)_2$ structure exist in narrowed phase fields in comparison to the β phase. The maximal doping of the α solid solution with RE amounts to ~3 mass%. This may not be sufficient active ion content in the α phase necessary to achieve a long-lasting phosphorescence or to apply the material in thermoluminescence dosimetry [47].

There are several similarities between the $\text{Ca}_3(\text{PO}_4)_2$ – YPO_4 and $\text{Ca}_3(\text{PO}_4)_2$ – CePO_4 systems [36]. Despite the difference between the CePO_4 (monazite) and YPO_4 structures (xenotime), concentration and temperature ranges of all phases in the systems are close to each other.

Conclusions

The phase diagram of the $\text{Ca}_3(\text{PO}_4)_2$ – YPO_4 system has been proposed in the revised form. The presented results

confirm existence of three fields of limited solid solution with β , α -, and α' - $\text{Ca}_3(\text{PO}_4)_2$ structure. At 1,100 °C the single-phase field of the YPO_4 solid solution in β - $\text{Ca}_3(\text{PO}_4)_2$ extends to ~15 mass% (~23 mol%). The high-temperature solid solutions form in narrowed concentration range in comparison to the β phase.

The doping by YPO_4 results in easier $\alpha \rightarrow \beta$ transformation than in pure $\text{Ca}_3(\text{PO}_4)_2$. The metastable α solid solution can be obtained only by quenching of samples with the low YPO_4 content. Since the doped material crack on cooling, obtaining of dense ceramic with the α structure is not possible.

The $\text{Ca}_3\text{Y}(\text{PO}_4)_3$ phosphate is a thermodynamically stable phase at temperature exceeding 1,255 °C, and it has one structural form.

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