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Phase transitions in amorphous calcium phosphates with different Ca/P ratios

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Abstract

The phase transitions occurring during calcination of flame-made calcium phosphates with Ca/P ratios between 1.00 and 1.54 were investigated by thermal analysis and powder X-ray diffraction from room temperature to 1350 °C. The as-prepared samples were amorphous and crystallized into metastable, low-temperature α_{LT} polymorphs of $Ca_3(PO_4)_2$ (TCP) and $Ca_2P_2O_7$ (CPP) between 600 and 700 °C, depending on the Ca/P ratio. The enthalpy changes during crystallization amounted to 26.1 and 58.5 J/g for TCP and CPP, respectively. The metastable α_{LT} TCP and CPP phases were at first transformed into stable β polymorphs between 870 and 950 °C and, later, between 1140 and 1200 °C, into high-temperature α phases. The enthalpy changes during these processes were small and lay in the range of 6–11 J/g. The composition of the eutectic formed in the system α-(TCP–CPP) was determined from the Tamman triangle, the melting enthalpy amounted to 197 J/g and the molar eutectic composition was 0.68 TCP and 0.32 CPP. The use of DSC analyses allowed to determine the composition of the precursor mixture during flame-made process which resulted in the synthesis of pure TCP amorphous phase.

Keywords: Calcium phosphates; Amorphous; Phase transitions; DSC; Eutectic; Heat of transition

1. Introduction

Amorphous calcium phosphates are the transient phases playing an important role in biomineralization processes of bone formation. Of particular interest for bone repair [1], coatings of metallic implants or abrasive agents in dentistry are the crystalline phases of tricalcium phosphate $Ca_3(PO_4)_2$ (TCP), hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ and calcium pyrophosphate $Ca_2P_2O_7$ (CPP). The properties of these materials are influenced by their phase purity and crystallographic form dependent on the synthesis method [2–6]. Such differences in material properties as higher reactivity of α-TCP than β-TCP in aqueous systems [5] or differences in biodegradability have an impact on the behavior of biomaterials once implanted into the human body. It is therefore necessary to understand better the processes of phase transitions of such materials to produce the calcium phosphates with required purity and phase composition.

The phase diagram of the $CaO–P_2O_5$ system in the range of the composition expressed by the Ca/P ratio between 1 (CPP) and 1.5 (TCP) shows the presence of only two phases having low-(β) and high-temperature (α) modifications. The α-polymorphs of TCP and CPP form an eutectic which melts around 1300 °C. However, the temperatures of the polymorphic transformations reported in the literature are not univocal, and the composition of the eutectic is not clearly described.

Amorphous calcium phosphates can be synthesized in aqueous solutions [7–10], by quenching the crystalline precursors calcined up to temperatures exceeding 1350 °C [11] or by the sol–gel process [12,13]. In order to investigate the phase transformation and thermal evolution of calcium phosphates with different Ca/P ratios it is advantageous to use an appropriate synthesis method which allows a precise control of the Ca/P ratio. Flame spray synthesis is the method of choice for this purpose since it allows an exact control thereof by appropriate metal loading of the precursor liquid [14,15].

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The purpose of this study was the determination of the thermal effects and temperatures of the phase transitions occurring in amorphous flame-made calcium phosphates during their calcination from room temperature to 1350 °C. Additionally, the composition and melting temperature of the eutectic in the system CPP–TCP was studied. The here presented results demonstrate that the synthesis of pure TCP phase requires a Ca/P ratio of 1.525 instead of stoichiometric value of 1.500.

2. Experimental

2.1. Sample preparation

Calcium phosphates with calcium to phosphorus (Ca/P) ratios from 1 to 1.575 were prepared using flame spray synthesis [16] and described in more detail by Loher et al. [17]. Calcium oxide (99.9%, Aldrich) dissolved in 2-ethylhexanoic acid (purum, ≥98%, Fluka) and tributyl phosphate (puriss ≥99%, Fluka) were mixed in the corresponding Ca/P ratios and used as precursor liquids. The calcium content of the Ca precursor was determined by complexometric titration with ethylenediaminetetraacetic acid disodium salt dihydrate (≥99%, Fluka) amounted to 0.77 mol Ca/kg calcium precursor solution The concentration of the precursor solutions was kept constant for all experiments (0.67 mol/L) by adding xylene (96%, Riedel de Haen). The liquid mixtures were fed through a capillary (diameter 0.4 mm) into a methane/oxygen flame at a rate of 5 mL/min. Oxygen (5 L/min, 99.8%, Pan Gas) was used to disperse the precursor solutions. The gas flows were controlled by calibrated mass flow controllers (Bronkhorst). The as-formed particles were collected on a glass fibre filter (Whatmann GF/A, 25.7 cm diameter), placed on a cylinder mounted above the flame, by the aid of a vacuum pump (Vacubrand).

2.2. Characterization techniques

XRD analysis was performed on a Siemens D5000 powder X-ray diffractometer using Cu Kα radiation with a step size of 0.01° and 2 s/step.

Simultaneous thermal analysis (TG and DSC)–MS and PulseTA, used for the quantification of evolved gases [18], were carried out on a Netzsch STA 409 (Germany) thermoanalyzer equipped with a pulse device enabling injection of a certain amount of one or two pure gases or gaseous mixtures into the carrier gas stream flowing through the system. The gas flow rate was controlled by mass flow controllers (Brooks model 5850E). The outlet of the thermoanalyzer was connected by a heated (ca. 150 °C) stainless steel capillary to mass spectrometer (Pfeiffer Vacuum OmniStar). The experiments were carried out in Ar atmosphere (flow 50 mL/min) in Pt crucibles with a heating rate of 10 °C/min. The samples mass was in the range of 60–70 mg. The empty crucible was used as a reference sample in DSC measurements.

The calibration of the temperature scale and the enthalpy calibration factors were done using as a standard the values obtained during the melting of In, Al and Au according to the IUPAC Technical Report concerning the calibration standards for DSC [19]. Additionally, for the temperature scale calibration the orthorhombic to hexagonal transformation of $BaCO_3$ was used [20]. The temperature calibration was done in an Ar atmosphere by recording the extrapolated peak onset temperature as a function of the heating rate and linear extrapolation to the heating rate $\beta = 0$ K/min. The temperature correction terms amounted to 0.8, 1.2, 2.0 and 1.8 K for the melting of In, Al and Au and polymorphic transformation of $BaCO_3$, respectively. The accuracy of the temperature values is therefore in the range of 1–2 K.

The values of the enthalpy change during the melting of the standards were 29.5; 388 and 62.6 J/g for the In, Al and Au, respectively. Comparing these values with those recommended in [19], i.e. 28.62 J/g for In, 399.9 J/g for Al and 64.58 J/g for Au we can state that the enthalpy calibration factors in the range 157–1064 °C amount to 1.00 ± 0.03 indicating that the uncertainty of the enthalpy values should not exceed ±3%.

The calibration of the DSC signals was done using a sapphire plate by the conventional heat capacity quantification procedure: the run with empty pans was followed by the run with sapphire allowing an exact determination of the relationship C_p–T used later for the determination of the enthalpy change due to the phase transitions.

The phase composition during temperature increase was monitored by the XRD analysis of the samples quenched at the required temperatures before and after the thermal events observed on DSC signal.

3. Results and discussion

To check the possible presence of carbonate phase in the samples the TG and MS signals ($m/z = 44$, CO_2) were monitored simultaneously with the DSC traces. The observed mass losses between RT-1300 °C were in the range of 2–3 wt% and resulted mainly from the evolution of the physisorbed water desorbed between RT and ca. 350 °C. The amount of evolved CO_2 was negligible: the total amount of CO_2 evolved was in the range between 0.05 and 0.64 wt% for the samples with Ca/P ratio of 1.425 and 1.5375, respectively.

The results of the XRD and thermal (TA) analyses of the sample with the composition Ca/P = 1.485 in the range 400–1350 °C are presented in Figs. 1 and 2, respectively.

The XRD phase analyses were performed with the samples heated until the temperatures marked by arrows on DSC signal, quenched and analyzed at room temperature. The as-received sample were X-ray amorphous showing two badly resolved peaks centered at ca. 30° and 45° having the widths of ca. 20 $2\theta°$.

The phase transitions depicted in Fig. 2 occurred in all samples with the ratio $1 < Ca/P < 1.5$.

In the DSC traces of the flame-made calcium phosphates one can distinguish the four temperature ranges described below in which the specific phase transitions occur.

3.1. Range 600–700 °C

The flame-made calcium phosphates were amorphous: the XRD analysis of the as-received samples and those collected

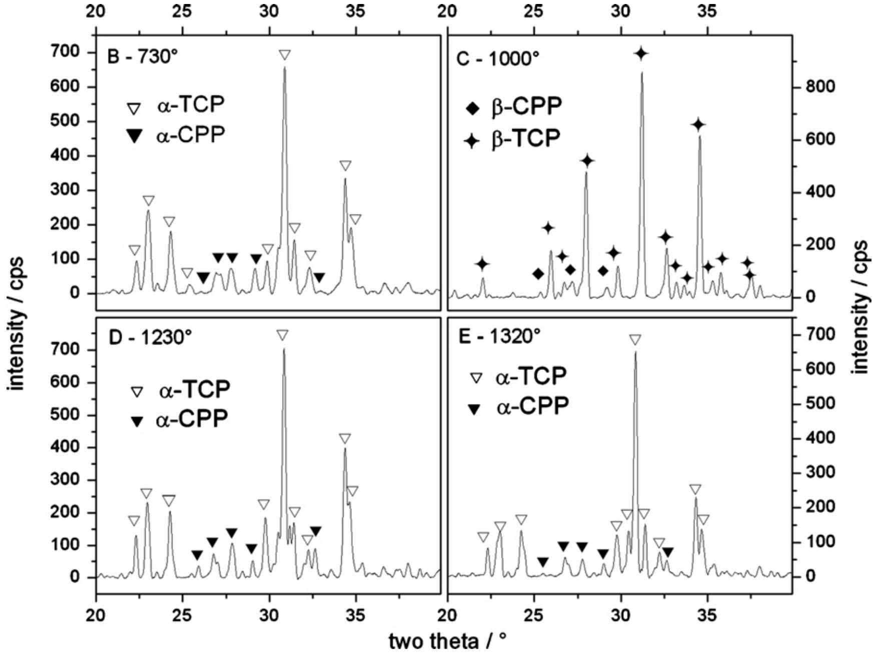

Fig. 1. XRD patterns of the samples collected at temperatures 730, 1000, 1230 and 1320 °C marked by B, C, D and E in Fig. 2, respectively.

during TA measurements before the first exothermal event (point A in Fig. 2) did not indicate any patterns characteristic for the crystalline phases, however, the presence of short-range ordering in the samples cannot be excluded as has been mentioned in Ref. [5]. The strong exothermic event visible on the DSC curve between 600 and 700 °C resulted from the crystallization of the amorphous phase and formation of the, at this temperature, metastable α-polymorphs of TCP (first) and CPP (second peak), respectively. These low-temperature (LT) α-metastable phases were labeled throughout the text as α_{LT} to distinguish them from the thermodynamically stable high-temperature polymorphs α-TCP and CPP. The formation of the α_{LT}-TCP from the amorphous phase above 600 °C was also reported for the quenched calcium phosphate by Somrani et al. [11] and Eanes [8] who found that the supersaturation during precipitation of amorphous calcium phosphate influences the ratio between α and β TCP forms after crystallization at ca. 600 °C.

The change of the composition of the samples influenced the temperature of the transformation of the amorphous material into α_{LT}: note the shift of the peak maximum temperature to lower temperatures when the Ca/P ratio increases (Fig. 3). On the other hand, the temperature of the transformation of the amorphous CPP phase into α_{LT}-CPP did not depend on the Ca/P ratio: the second, sharper exothermic peak caused by this reaction occurs at the same temperature in all samples.

Surprisingly, the crystallization of the amorphous phase in pure samples was significantly shifted to lower temperature: the maxima of the transition of the amorphous phase into α_{LT} phases

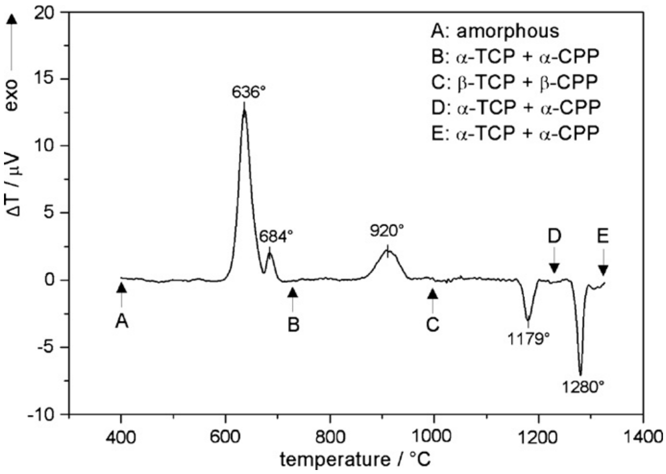

Fig. 2. DSC signal of the amorphous flame-made calcium phosphate with the composition Ca/P = 1.485. The inset presents the results of the phase analysis of the samples collected at temperatures marked on DSC curve.

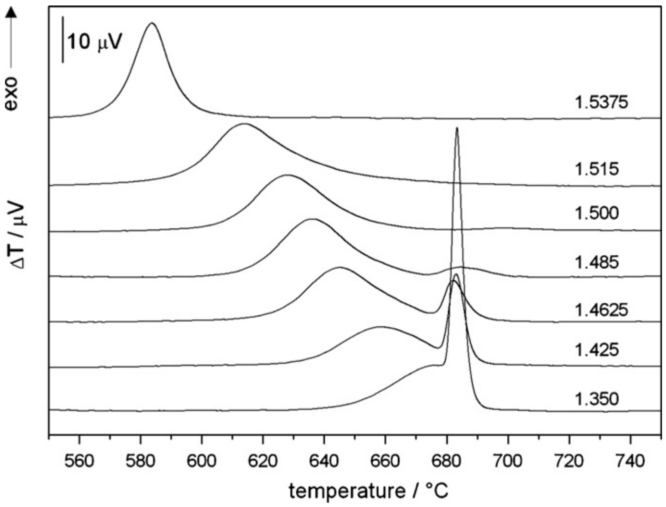

Fig. 3. DSC curves of the flame-made calcium phosphates depicting the transformation of amorphous as-received samples into the metastable α forms (α_{LT}) of TCP and CPP. The Ca/P ratios are marked on the curves.

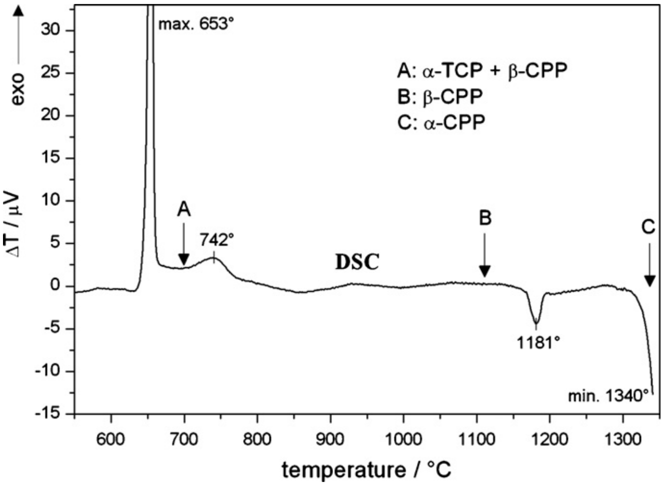

Fig. 4. DSC traces of flame-made $Ca_2P_2O_7$. The inset presents the results of the phase analysis of the samples collected at temperatures marked on DSC curve.

are significantly shifted to lower temperatures for pure TCP (sample with Ca/P 1.5375, Fig. 3) and pure CPP (Fig. 4). The observation that the presence of CPP phase inhibited the crystallization of the amorphous TCP prepared by the precipitation has been previously reported by Fleisch et al. [10]. The temperatures of all phase transformations and their enthalpy changes are summarized in Table 1.

3.2. *Range 850–950 °C*

The weaker exothermic event occurring in the range 850–950 °C was due to the transformation of the metastable α_{LT}-TCP into β-TCP which was thermodynamically stable at this temperature. Because of the small amount of CPP in the samples the transformation of the α_{LT}-CPP into at this temperatures stable β-CPP was observed only with the samples containing larger amount of CPP, i.e. having lower Ca/P ratio. The DSC trace of the pure, flame-made CPP are presented in Fig. 4 showing that α_{LT}–β transition occurred with a small exothermic event in the range of ca. 650–800 °C (maximum centered at 742 °C).

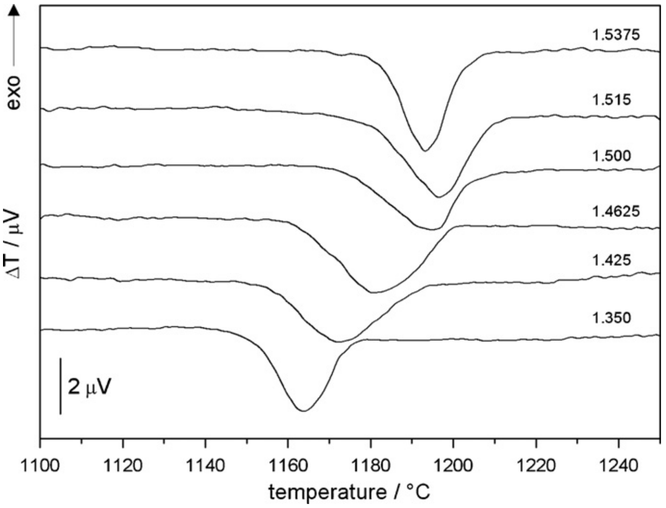

Fig. 5. DSC curves of the flame-made calcium phosphates showing the transformation of β-TCP and CPP into at this temperature thermodynamically stable α-TCP and CPP. The corresponding Ca/P ratios are assigned to the curves.

3.3. *Range 1140–1200 °C*

Above 1000 °C the flame-made calcium phosphates contained the low temperature forms of β-TCP and β-CPP (at these temperatures thermodynamically stable). The endothermic events observed in the range of 1140–1200 °C resulted from the β–α transformations of TCP and CPP and are presented in Fig. 5. According to previous studies the thermodynamically stable low temperature (β) CPP polymorph transforms to high-temperature α form at 1120° [21], 1125° [22], 1140° [23], 1155° [24], 1202° [25] and melts at 1300 °C [22], 1330 °C [24]. TCP shows the β–α transition at 1125° [23], 1135° [24], 1150° [26], 1160° [27], 1200° [21], above 1200° [28] and 1350° [29] and as a melting point the temperatures 1735 °C [22], 1770 °C [24] and 1777 °C [23] were reported. It is comprehensible that due to the very small difference between the temperatures of the β–α transitions of TCP and CPP they are not separated in DSC traces and both transitions occur simultaneously in the form of a single peak. Additionally, the determination of very small changes of the enthalpy due to the transformation of the thermodynamically unstable α_{LT} into β polymorphs and their further transformation

Table 1
Temperatures of the maxima and the heat (J/g) of the phase transformations as a function of the composition of the flame-made calcium phosphates

Ca/P ratio	Amorphous → α_{LT}-TCP		Amorphous → α_{LT}-CPP		α_{LT}-TCP → β-TCP		β-TCP → α-TCP, β-CPP → α-CPP		Melting of eutectic and CPP	
	°C	J/g	°C	J/g	°C	J/g	°C	J/g	°C	J/g
1.5375	584	−22.2	–	–	889	−7.7	1193	10.6	–	–
1.515	614	−26.1	–	–	920	−8.2	1196	11.4	1284	6.5
1.500	627	−24.6	–	–	917	−6.2	1194	9.7	1276	12.3
1.485	636	−24.7	684	−2.3	920	−10.1	1179	11.4	1280	24.8
1.4625	645	−22.6	682	−4.0	924	−9.7	1180	10.4	1294	35.2
1.425	658	−19.5	683	−7.2	924	−7.9	1171	9.3	1293	61.2
1.350	674	−16.5	683	−15.1	925	−5.0	1162	7.5	1300	92.3
1.000	–	–	653	−58.5	742[a]	−6.9[a]	1181	11.9	–	–

[a] Transformation α_{LT}-CPP → β-CPP.

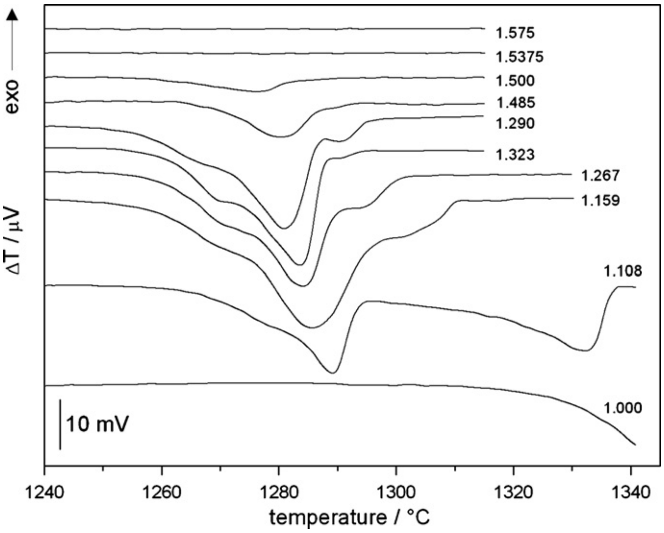

Fig. 6. DSC signals resulting from melting eutectic and crossing liquidus curve in the system TCP–CPP.

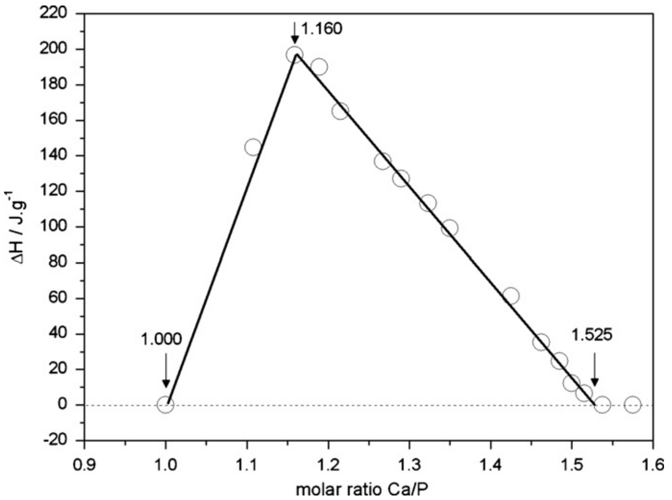

Fig. 7. Tamman triangle: the dependence of the heat of the eutectic melting on the composition of the calcium phosphates.

into thermodynamically stable α forms is difficult because of the low sensitivity of the DSC signals at temperatures exceeding 1000 °C.

3.4. Range 1240–1340 °C

After the endothermic β–α transition (point D in Fig. 2) both phosphates were present in α form. According to the published phase diagrams in the system TCP–CPP an eutectic occurs with approximate melting temperature of 1280 °C [13,14], 1287 °C [23] and 1300 °C [24] and with molar composition of ca. 0.66 CPP. The thermal effects presented in Fig. 6 represent the melting of the eutectic (1284 ± 5 °C) followed by the endothermic shoulder (peak) due to the crossing liquidus curve.

Samples which did not contain TCP or CPP (samples with Ca/P = 1.000 and 1.5375, respectively) the eutectic was not formed. Surprisingly, the sample with the composition 1.500 which should contain pure TCP phase showed a small endothermic peak due to melting of the eutectic, formed due to the presence of the traces of CPP. In order to check the composition of the eutectic systematic studies of the dependence of the enthalpy changes resulting form the eutectic melting versus sample composition were undertaken. Such a dependence, known as Tamman triangle allows the exact determination of the eutectic composition. The values of the heat of melting were determined from the DSC traces presented in Fig. 6 after signal fitting by multiple Lorentzian peaks and removal from the total recorded heat the contribution resulting from the crossing liquidus curve (high temperature shoulder overlapping main peak of eutectic melting). The values of the heat of the eutectic melting as a function of the Ca/P ratio are shown in Fig. 7.

It could be shown that the highest ΔH_{eut} value, indicating the eutectic composition, was found for the ratio Ca/P = 1.16 which is equivalent to the molar composition of 0.68 TCP and 0.32 CPP.

The heat of the melting amounted to 197 J/g. The results depicted in Fig. 7 indicated that pure TCP can be synthesized by means of the flame-method under the applied conditions when the ratio of Ca/P in the precursor liquid mixture is equal to 1.525. The synthesis using a stoichiometric ratio of 1.5 resulted in materials containing traces of CPP.

4. Conclusion

Within this study we have systematically studied the phase transitions of flame-derived calcium phosphates. The temperature ranges of the stability of different intermediate polymorphs and the values of the heat of the transitions occurring during thermal evolution of amorphous calcium phosphates have been elucidated. The results indicate that due to the high rate of quenching during synthesis, the flame-made calcium phosphates are amorphous. The crystallization takes place at relatively high temperatures between 580 and 670 °C, depending on the Ca/P ratio. The values of the crystallization enthalpy, corresponding to the amorphous-crystalline transformation, amount to 26.1 J/g (8.1 kJ/mol) for TCP and 58.5 J/g (14.9 kJ/mol) for CPP, respectively. Kumar et al. [30] and Feng et al. [31] have reported the values of the heat of crystallization of the ACP into hydroxyapatite being equal to 43.0 and 20.9 kJ/mol, respectively.

Initially metastable high temperature α-polymorphs of CPP and TCP, labeled here as α_{LT} phases, were formed which transformed exothermally into thermodynamically stable β-phases in the range 890–925 °C. The transformation α_{LT} into β phase in pure flame-made CPP occurs at ca. 740 °C.

At about 1180–1190 °C the β-CPP and β-TCP phases transformed into at this temperatures thermodynamically stable α-CPP and α-TCP polymorphs. A precise calibration of the DSC signal allowed estimating these enthalpy changes to be in the range of 6–11 J/g (2–3 kJ/mol).

The temperature of the maximum of the eutectic melting peak under the applied heating rate (10 K/min) was found to be 1286 °C, the heat of the eutectic melting: 197 J/g, and the eutectic molar composition determined from the Tamman triangle: 0.68 TCP and 0.32 CPP.

The very sensitive DSC technique applied revealed that the sample synthesized by the flame-method using a stoichiometric ratio Ca/P = 1.5 contained traces of CPP giving rise to the formation of a small amount of eutectic. Detection of such a small amount of the second phase is impossible by XRD. To obtain the pure TCP phase one has to change the composition of the reactants: the pure phase, as determined from the Tamman triangle, is obtained when the Ca/P ratio in the precursor mixture amounts to 1.525.

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