



## Preparation of calcium polyphosphate powder containing amorphous carbon

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Uniform dark grey colored powders of  $\beta$ -calcium polyphosphate  $\beta$ -Ca(PO<sub>3</sub>)<sub>2</sub> with fine particles (2–4  $\mu$ m) modified with amorphous carbon were prepared using heat treatment of monocalcium phosphate monohydrate Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O after treatment in water solution of lactic acid CH<sub>3</sub>CHOHCOOH under mechanical activation using planetary mill. Prepared dark grey coloured powders of calcium polyphosphate can be used as a multifunctional additive in technology of porous calcium phosphate ceramics using stereolithographic printing as a molding method of semi-finished items.

Keywords: Monocalcium phosphate monohydrate, lactic acid, calcium polyphosphate powder.

### Introduction

According to existing phase diagrams and experience of different research groups it is possible to produce ceramic materials or composites in CaO-P<sub>2</sub>O<sub>5</sub> system with restricted number of biocompatible crystalline phases<sup>1,2</sup>. They are oxyapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>O (hydroxyapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub>) with molar ratio Ca/P = 1.67, tricalcium phosphate Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> with molar ratio Ca/P = 1.5, calcium pyrophosphate Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> with molar ratio Ca/P = 1 and calcium polyphosphate Ca(PO<sub>3</sub>)<sub>2</sub> with molar ratio Ca/P = 0.5. Calcium phosphate materials with molar ratio Ca/P < 1.67 are bioresorbable and can be dissolved in body fluids when implanted. Calcium polyphosphate Ca(PO<sub>3</sub>)<sub>2</sub> as a component of starting powder mixtures can be used as a low temperature sintering additive when creating a ceramics in CaO-P<sub>2</sub>O<sub>5</sub> system<sup>3</sup>. Calcium polyphosphate Ca(PO<sub>3</sub>)<sub>2</sub> can interact with other calcium phosphates, calcium oxide or precursors of calcium oxide such as calcium carbonate or calcium hydroxide to form another calcium phosphates<sup>4</sup>. For example, if we mix the calcium polyphosphate Ca(PO<sub>3</sub>)<sub>2</sub> and calcium hydroxyapatite Ca<sub>10</sub>(PO<sub>4</sub>)<sub>6</sub>(OH)<sub>2</sub> in specified quantities, we can get calcium pyrophosphate Ca<sub>2</sub>P<sub>2</sub>O<sub>7</sub> or tricalcium phosphate Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> in the phase composition of ceramics<sup>5</sup>.

Resorbable calcium phosphate ceramics intended for use in regenerative methods of treating bone defects must be

macroporous<sup>6</sup>. Stereolithographic printing of a semi-finished ceramic item is a molding method in technology of ceramics with a given geometry of the pore space<sup>7</sup>. Due to the scattering of light on the white inorganic particles in the light-cured suspension of monomers, the print resolution is poor<sup>8</sup>. As a dye, carbon-coloured powders can improve the lateral resolution of printing<sup>9</sup>.

The aim of the present study consisted in developing of method of preparing of calcium polyphosphate powder Ca(PO<sub>3</sub>)<sub>2</sub> modified with amorphous carbon.

### Experimental

10 g of monocalcium phosphate monohydrate Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O powder (CAS no. 10031-30-8 puriss. p.a.  $\geq$  85%, Sigma-Aldrich), 10 ml of 4 M solution of lactic acid prepared from 80% solution of lactic acid (OOO Rushim, GOST 490-2006) and 50 g of grinding media (zirconia balls) were placed in a container made from zirconia. The container with monocalcium phosphate monohydrate Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>·H<sub>2</sub>O powder, solution of lactic acid and grinding media were closed and fixed in a planetary mill (Fritch, Germany). The duration of mechanical activation of powder at a rotation rate of 600 rpm was 15 min. After mechanical activation using planetary mill transparent solution including lactic acid and monocalcium phosphate monohydrate

$\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  was dried in air at room temperature for one week. After drying, the powder were heat treated in a furnace at 400 and 500°C (the heating rate was 5°C/min, holding for 1 h at the specified temperature, and cooling together with furnace).

The X-ray powder diffraction study (XRD) of the powders before and after mechanical activation and as well as after annealing was performed on a Rigaku D/Max-2500 rotating anode diffractometer (Japan) using  $\text{CuK}\alpha$  radiation. The qualitative phase analysis was performed using the ICDD PDF2 database<sup>10</sup>.

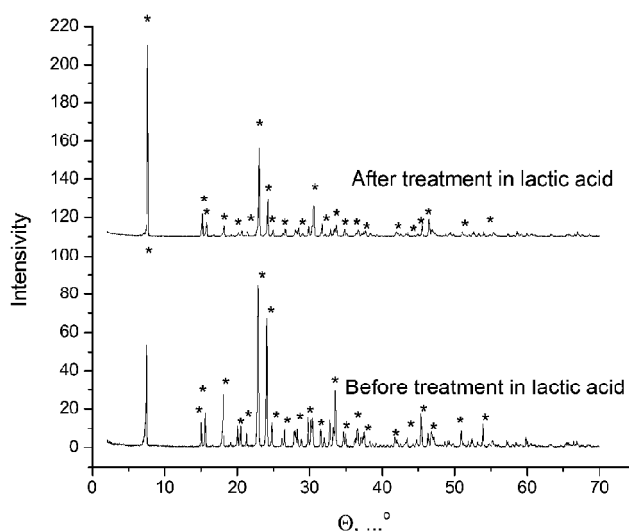
Synchronous thermal analysis was performed on a NETZSCH STA 409 PC Luxx thermal analyzer (NETZSCH, Germany) in a temperature range from 40 to 1000°C at a heating rate of 10°C/min. The sample weight was at least 10 mg. The composition of the gas phase formed upon decomposition of samples was studied using a QMS 403C Aëolos quadrupole mass spectrometer (NETZSCH, Germany) coupled to the NETZSCH STA 409 PC Luxx thermal analyzer. Mass spectra were recorded at  $m/z$  18 and 44 (corresponds to  $\text{H}_2\text{O}$  and  $\text{CO}_2$ ).

The microstructure of the samples was studied by using LEO SUPRA 50VP electron microscope (Carl Zeiss, Germany; field-emission source); recording was implemented at an accelerating voltage of 3–20 kV in the mode of secondary electrons (SE2 detector). A chromium layer (up to 10 nm) was deposited onto the sample surface.

## Results and discussion

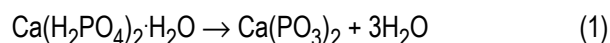
Powder of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  was dissolved in water solution of lactic acid during treatment under mechanical activation using planetary mill.

According to XRD analysis data (Fig. 1) the phase composition of powder after crystallisation from this solution and drying at room temperature was the same as a phase composition of the starting monocalcium phosphate monohydrate powder. Particle dimensions of monocalcium phosphate monohydrate after mill treatment, crystallisation in presence of lactic acid and drying changed from 100–300  $\mu\text{m}$  to 10–50  $\mu\text{m}$  (Fig. 2). So, lactic acid acted as surface active agent during crystallisation of particles of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  from the solution.



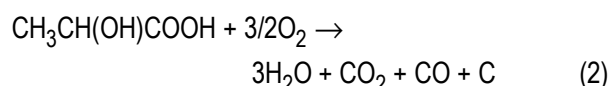
**Fig. 1.** XRD data for monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  powder before and after treatment in water solution of lactic acid under conditions of mechanical activation using planetary mill and followed by crystallization: \* - PDF card # 9-347.

The total mass loss of the starting powder of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  at 1000°C was 22% according to thermal analysis data (Fig. 3). And this value of mass loss corresponds to the calculated value according to reaction (1).

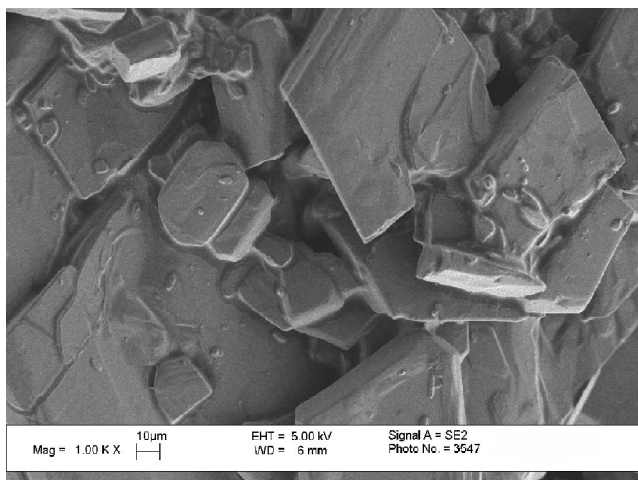


The total mass loss of powder of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ , containing lactic acid, at 1000°C was 38% according to thermal analysis data (Fig. 3). The total mass loss of the powder of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  containing lactic acid was due to decomposition of both inorganic and organic components.

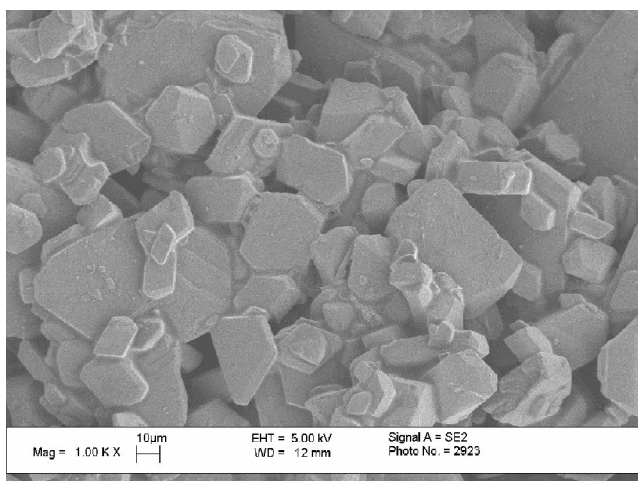
The reactions (1) and (2) summarise the chemical transformation taking place during heat treatment of powder of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  containing lactic acid.



The mass spectrometric curves given for  $m/z$  18 ( $\text{H}_2\text{O}$ ) (Fig. 4a) suggest that the decomposition of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  pass through three



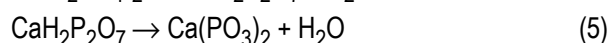
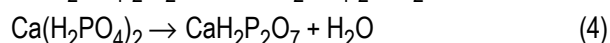
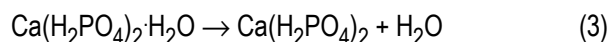
(a)



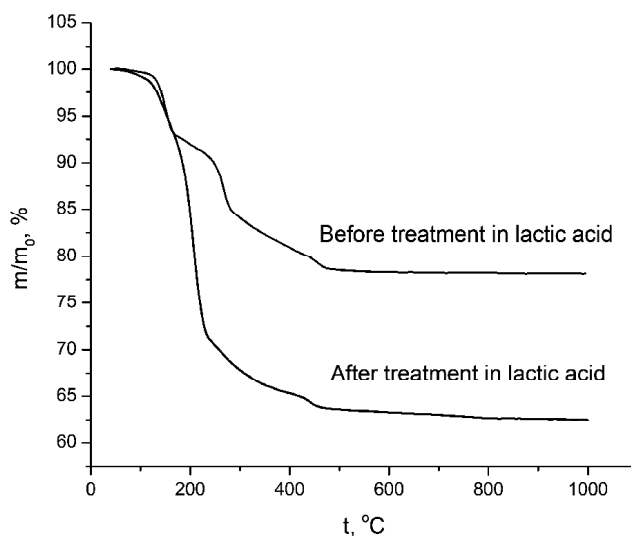
(b)

**Fig. 2.** Micrographs of powders of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  powder before (a) and after (b) treatment in water solution of lactic acid under conditions of mechanical activation using planetary mill and followed by crystallization.

stages:  $\sim 100\text{--}200^\circ\text{C}$ ,  $\sim 230\text{--}350^\circ\text{C}$  and  $430\text{--}500^\circ\text{C}$ . So the mass loss at these stages can be reflected with the following reactions:



The mass spectrometric curves for powder of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  containing lactic acid given for  $m/z$  18 ( $\text{H}_2\text{O}$ ) (Fig. 4a) differs from mass



**Fig. 3.** Thermal analysis data for powders of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  powder before and after treatment in water solution of lactic acid under conditions of mechanical activation using planetary mill and followed by crystallization.

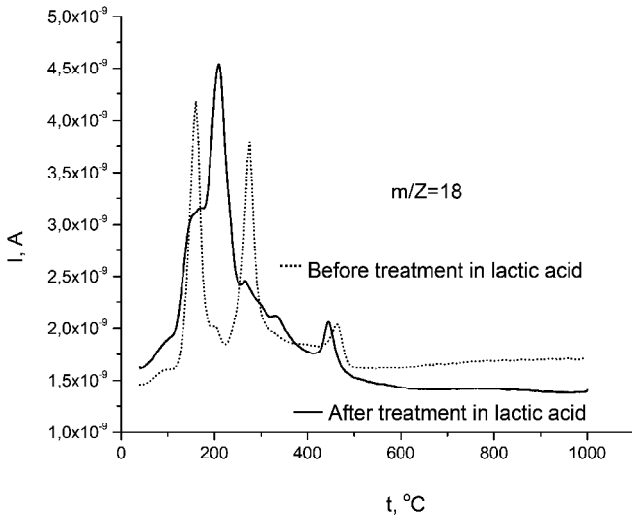
spectrometric curves for starting powder of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ . A broad peak in interval  $40\text{--}400^\circ\text{C}$  reflects the complicated decomposition of lactic acid and two first stages of decomposition of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  (reactions (3) and (4)). The interval ( $420\text{--}500^\circ\text{C}$ ) for reaction (5) at the mass spectrometric curves for powder of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  containing lactic acid is almost the same as the interval for reaction (5) at the mass spectrometric curves for monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  without lactic acid.

According to mass-spectrometry data (Fig. 4b) there were two intervals of carbon dioxide evolving:  $100\text{--}400^\circ\text{C}$  and  $900\text{--}1000^\circ\text{C}$ . It means that amorphous carbon can be kept in the powder of calcium polyphosphate  $\text{Ca}(\text{PO}_3)_2$  up to the quite high temperatures.

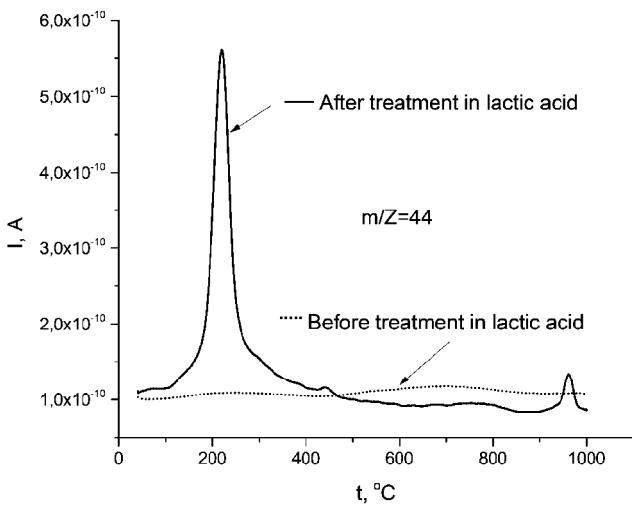
Photos of powders after heat treatment at  $400^\circ\text{C}$  and  $500^\circ\text{C}$  are presented at Fig. 5. Powders had dark grey color.

According to XRD analysis data powder after heat treatment at  $400^\circ\text{C}$  and  $500^\circ\text{C}$  consisted of  $\beta$ -calcium polyphosphate  $\beta\text{-Ca}(\text{PO}_3)_2$  (Fig. 6).

The microstructure of calcium polyphosphate  $\text{Ca}(\text{PO}_3)_2$  powders is shown in Fig. 7. Uniform dark grey colored cal-



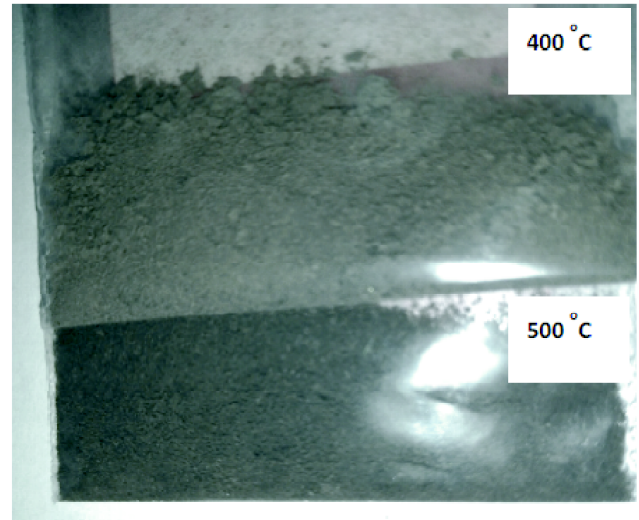
(a)



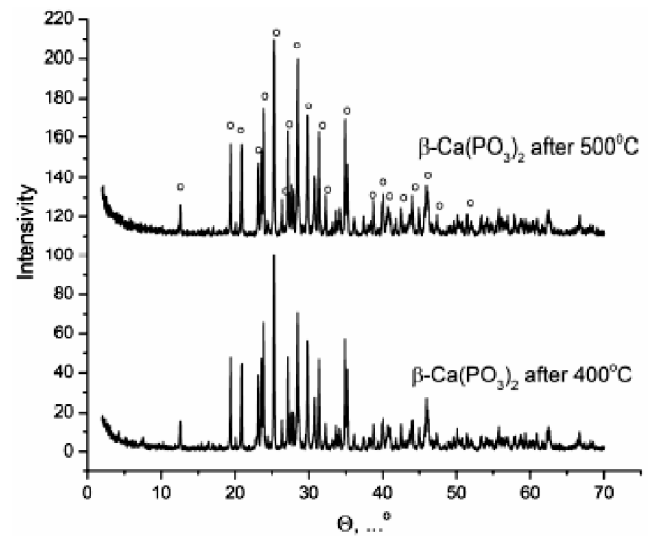
(b)

**Fig. 4.** Mass-spectrometry data for powders of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  powder before and after treatment in water solution of lactic acid and followed by crystallization for  $m/z = 18$  (a) and  $m/z = 44$  (b).

cium polyphosphate powder with fine particles (2–4  $\mu\text{m}$ ) was prepared using heat treatment of monocalcium phosphate

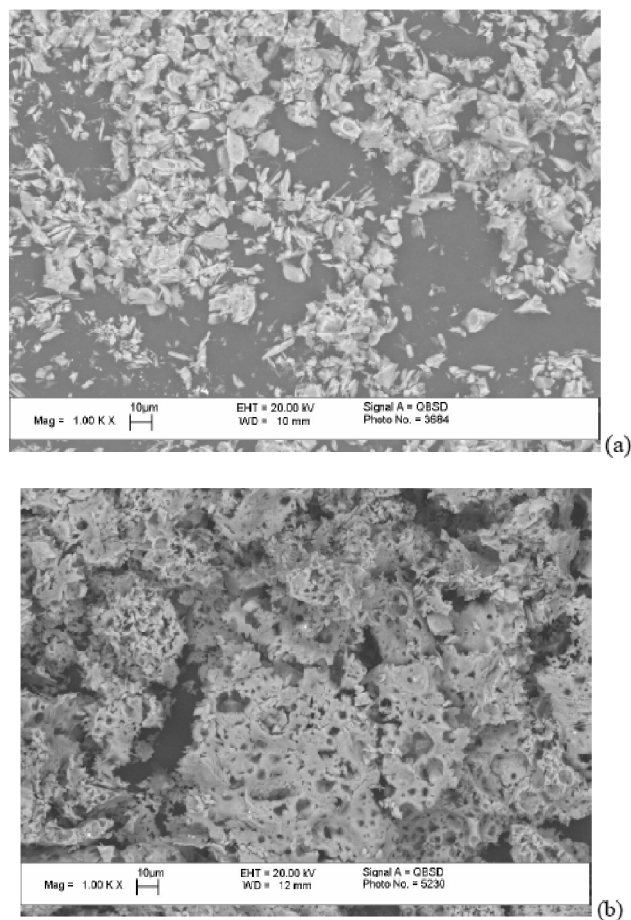


**Fig. 5.** Photos of powders of  $\beta$ -calcium polyphosphate  $\beta\text{-Ca}(\text{PO}_3)_2$  after heat treatment at 400°C and 500°C.



**Fig. 6.** XRD data for powders after heat treatment at 400°C and 500°C:  $\circ$  –  $\beta\text{-Ca}(\text{PO}_3)_2$  (PDF card # 81-2257).

monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  containing lactic acid (Fig. 7).



**Fig. 7.** Micrographs of  $\beta$ -calcium polyphosphate ( $\beta$ - $\text{Ca}(\text{PO}_3)_2$ ) powders after heat treatment at  $400^\circ\text{C}$  (a) and at  $500^\circ\text{C}$  (b) of powder of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  containing lactic acid.

## Conclusions

Monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  containing lactic acid was used for preparation of dark grey colored powders of  $\beta$ -calcium polyphosphate  $\beta$ - $\text{Ca}(\text{PO}_3)_2$ . Homogeneous distribution of both monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  and lactic acid were provided with treatment in planetary mill. It was shown that lactic acid can act as a surface active agent during crystallisation of monocalcium phosphate monohydrate  $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O}$  from solution formed after mechanical activation treatment.

Due to dark grey colour the powders of  $\beta$ -calcium polyphosphate  $\beta$ - $\text{Ca}(\text{PO}_3)_2$  can be an agent improving lateral resolution of 3D stereolithographic printing as molding method of semi-finished items with given geometry of porous space.

And due to the low melting point ( $964^\circ\text{C}$ ) prepared powders of  $\beta$ -calcium polyphosphate  $\beta$ - $\text{Ca}(\text{PO}_3)_2$  can be an additive giving opportunity to make the firing temperature of calcium phosphate ceramics lower.

Prepared dark grey coloured powders of  $\beta$ -calcium polyphosphate  $\beta$ - $\text{Ca}(\text{PO}_3)_2$  can be used as a multifunctional additive in technology of porous calcium phosphate ceramics using stereolithographic printing as molding method of semi-finished items.

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