



Ceramics based on calcium pyrophosphate nanopowders

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Abstract

Present work is aimed at the fabrication of resorbable bioceramics based on calcium pyrophosphate (CPP) from the synthesized powders of amorphous hydrated calcium pyrophosphate (AHCPP). Amorphous hydrated calcium pyrophosphate in the form of nanopowders was precipitated from $\text{Ca}(\text{NO}_3)_2$ and $(\text{NH}_4)_4\text{P}_2\text{O}_7$ solutions at room temperature in the presence of PO_3^- ions. Crystalline CPP powder was fabricated from AHCPP by its thermal decomposition at 600 °C and consisted of β - and α - phase. Small particles, with the size less than 200 nm, were formed promoting sintering of the ceramic material. The final sample, sintered at 900 °C, exhibits microstructure with submicron grains, apparent density of 87% of theoretical density (TD) and demonstrates tensile strength of 70 MPa.

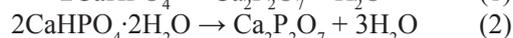
Keywords: calcium pyrophosphate, amorphous materials, nanopowders, bioceramics

I. Introduction

Nowadays the investigation of calcium phosphates is closely connected with the search for new materials capable of repairing and treating diseased bone tissue. Much attention is paid to hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, HAp) since it is the major constituent of the mineral part of the human skeleton. The use of pure HAp as bioceramics is quite inefficient since the material exhibits low *in vivo* resorption rate. That is why the development of resorbable materials or resorbable/resistive composite materials based on various calcium phosphates is the main stream of research activity in the field of bioceramics. One of the promising forms of calcium phosphates is calcium pyrophosphate ($\text{Ca}_2\text{P}_2\text{O}_7$, CPP).

It is worth noting that the preparation of calcium pyrophosphate ceramics is not trivial due to the phase transformation of CPP from β - into α -form at relatively low temperature (1140–1179 °C) [1], accompanied by volume increase of about 6%. The temperature of the transformation is not sufficient to lead to dense and strong ceramics. One of the ways to overcome this obstacle lies in the low-temperature synthesis of powder active in the sintering process.

CPP can be prepared by the wet precipitation method [2], solid state reaction [3], thermal decomposition of dicalcium phosphate dehydrate (DCPD, brushite, $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) or dicalcium phosphate (DCP, monetite, CaHPO_4) [4] and glass crystallization [5]. The formation of large particles with rather perfect crystallinity is usually observed in the solid state synthesized powders. Therefore, these powders are not useful for ceramic production. One of the most widespread methods of CPP formation is the thermal decomposition of monetite (reaction 1) or brushite (reaction 2) precipitated from solutions. Plate-like micromorphology and particle size of about 10 μm are typical for brushite and monetite, and after thermal decomposition CPP particles retain these characteristics.



There are literature reports on amorphous calcium pyrophosphate precipitate formation from calcium and pyrophosphate solutions [6]. Aging of the precipitate in the mother liquor results in the crystallization of calcium pyrophosphate hydrates with plate-like particles, 20 μm in size. Zn and Mn ions inhibit crystallization of the amorphous precipitate [7,8]. Amorphous powders composed of small equiaxed particles with defective structure are

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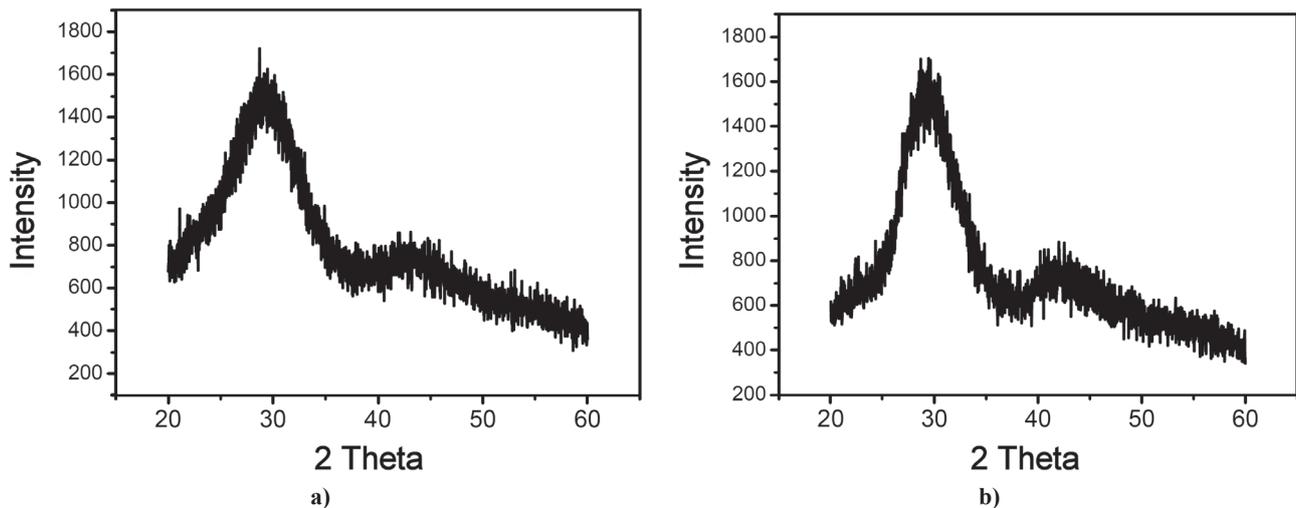


Figure 1. XRD patterns of as-synthesized AHCPP powders: a) as-received and b) aged in mother liquor during 24 hours

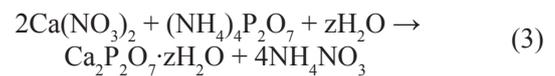
attractive for the preparation of ceramics by the conventional sintering procedure. In this paper, we describe the synthesis of amorphous calcium pyrophosphate powders and subsequent fabrication of CPP bioceramics.

II. Experimental

Ammonium pyrophosphate and calcium nitrate tetrahydrate were used as received from Labteh, Russia. The ammonium pyrophosphate powder contained about 5–10 % of ammonium polyphosphate according to the quantitative XRD analysis.

The powders of amorphous calcium pyrophosphate (AHCPP) were obtained via wet precipitation technique, by adding 157 ml of aqueous ammonium py-

rophosphate solution (0.5 M) to 315 ml of solution containing calcium nitrate (0.5 M) according to the following equation:



During precipitation, the pH level of the reaction zone was in interval 4.0–4.5. In order to study the influence of synthesis conditions on crystallization process the precipitated AHCPP particles were aged in mother liquor for different time (up to 72 hours).

The resulting precipitate (the as-synthesized AHCPP powder) was dried at room temperature during 48 hours. Dry powder was disaggregated by ball milling (3 min, acetone media, the ratio liquid : powder : balls was set to 2:1:5). The milled powder was passed through the sieve (Saatilene HiTech™ polyester fabrics, cells of 200 μm) and placed into the hot furnace to 600 °C for 15 min. The compacted samples of thus treated powder and the as-synthesized AHCPP powder were obtained by uniaxial pressing under 100 MPa in a stainless steel die into 6×40 mm rectangular bars. Sintering of the compacted samples made from the as-synthesized AHCPP powder was done at temperatures 300–900 °C with dwell time of 2 hours. Sintering of the compacted powder samples made from powders heat treated at 600 °C was done at temperatures 900–1100 °C with holding for 6 hours at maximum temperature. The heating rate was set to 5 °C/min for all the experiments.

XRD patterns were collected with CuKα radiation using D/Max-2500 (Rigaku, Japan). The microstructure of the powders and dense specimens were observed by FESEM at 5–20 kV (LEO Supra 50 VP, Carl Zeiss, Germany) and TEM at 200 kV (JEM-2000 FXII, JEOL, Japan). TGA of the specimens was conducted with Diamond Pyris (Perkin Elmer, USA) in air up to 1100 °C at heating rate of 5 °C/min. Flexural strength of ceramics was evaluated with the help of UTS Telesysteme GmbH

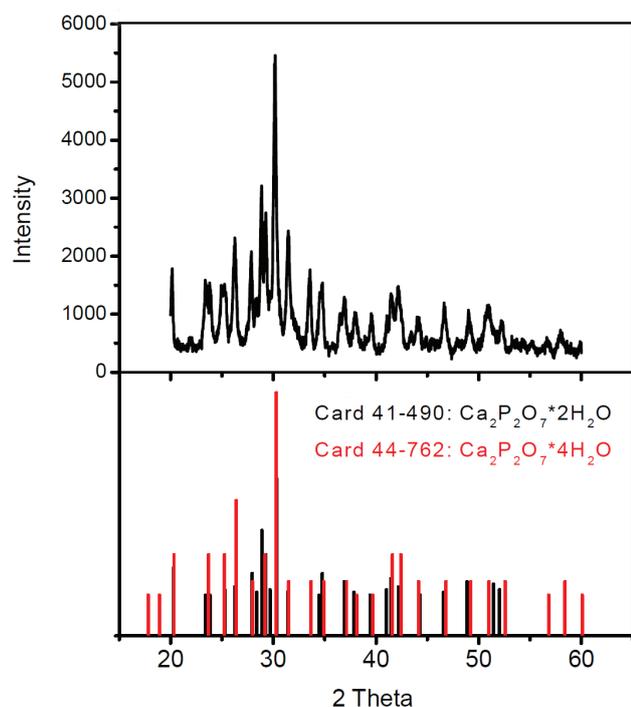


Figure 2. XRD of as-synthesized AHCPP powders after aging at mother liquor during 72 hours

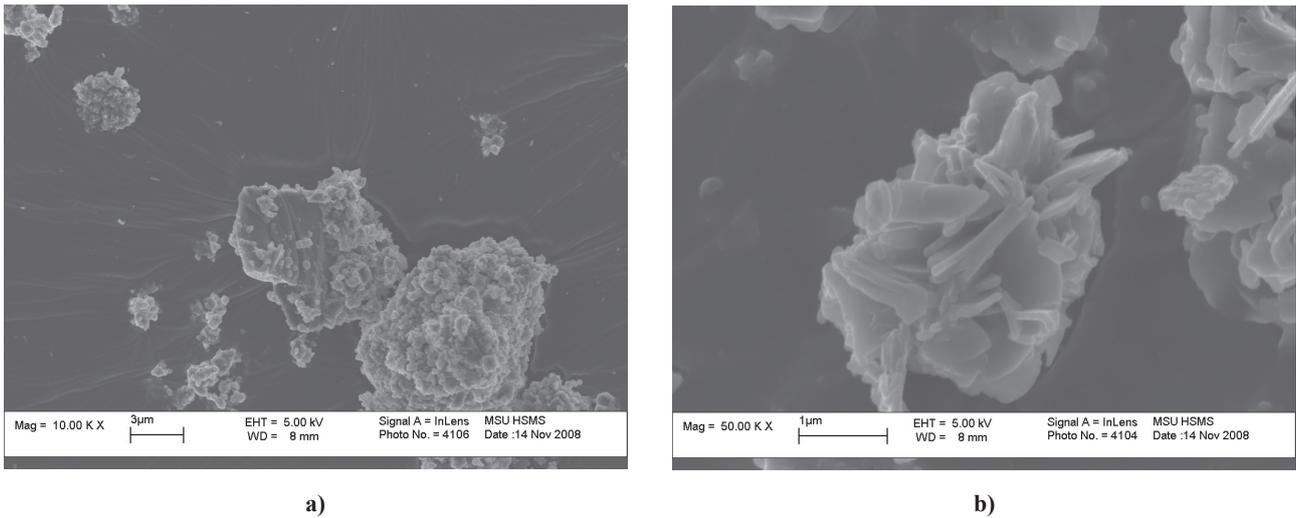


Figure 3. SEM microphotographs of as-synthesized AHCPP powders after aging at mother liquor during: a) 24 and b) 72 hours

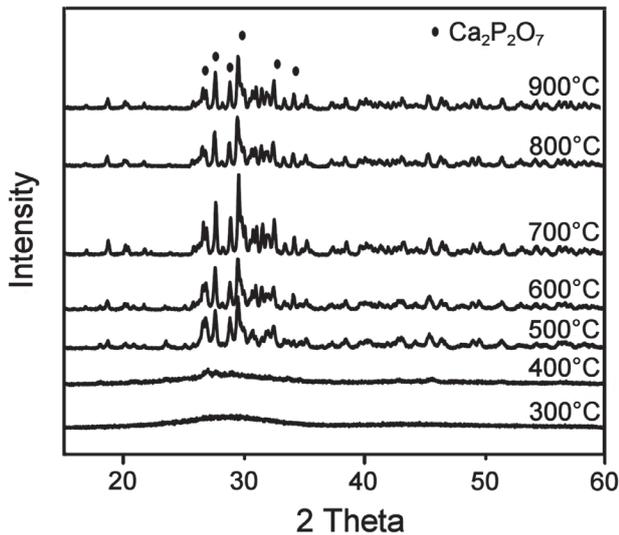


Figure 4. XRD patterns of AHCPP sample heated at different temperatures in interval 300–900 °C for 2 hours

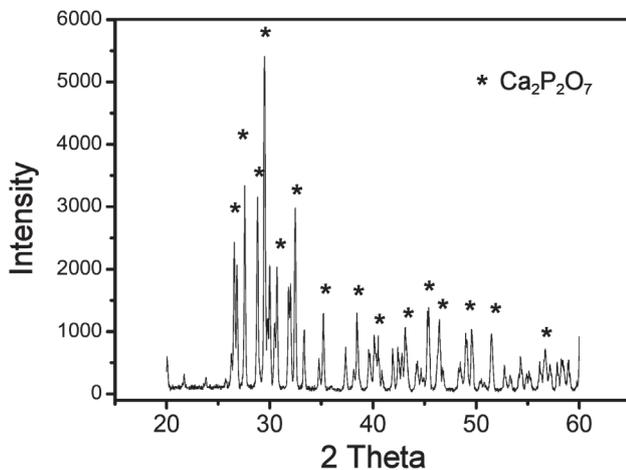


Figure 5. XRD pattern of AHCPP sample heated at 1100 °C for 2 hours

testing machine, Germany, without additional polishing. In order to study the statistical aspect of strength, 5 to 6 samples were tested.

III. Results and discussion

According to XRD the as-synthesized powder consists of amorphous (or very fine, nanocrystalline) calcium pyrophosphate particles (Fig. 1a). Apparent density of the as-synthesized powders after disaggregation was 0.3 g/cm³. Density of the green body after pressing was 1.4 g/cm³.

There are no peaks of CPP hydrates observed in the XRD patterns for the samples aged in mother liquor for 24 hours (Fig. 1b). However, after 72 hours of aging, the transformation of amorphous phase into the mixture of Ca₂P₂O₇·2H₂O and Ca₂P₂O₇·4H₂O is complete (Fig. 2). This fact is in agreement with SEM images that show that after 24 hours aggregates of sphere particles are formed (Fig. 3a) and after 72 hours of aging only plate-like particles remain (Fig. 3b). These plate-like particles often form clusters with typical dimensions from 1 to 10 μm.

XRD patterns of the AHCPP samples heated at different temperatures, presented in Fig. 4, clearly show that transformation from amorphous to crystalline form takes place at 400–500 °C. It should be outlined that Ca/P ratio of the precipitate is rather close to 1 since β-CPP is observed for the precipitates annealed at 1100 °C (Fig. 5).

The precipitate AHCPP powder consists of equiaxed particles with the size below 200 nm (Fig. 6a). These particles are quite sinterable even at temperatures as low as 600 °C (evidenced by the growing necks between particles, Fig. 6b). The thermal treatment of the precipitate leads to the decomposition of the by-product of AHCPP precipitation - NH₄NO₃, and to release of the adsorbed and chemically bonded water. According to TGA (Fig. 7)

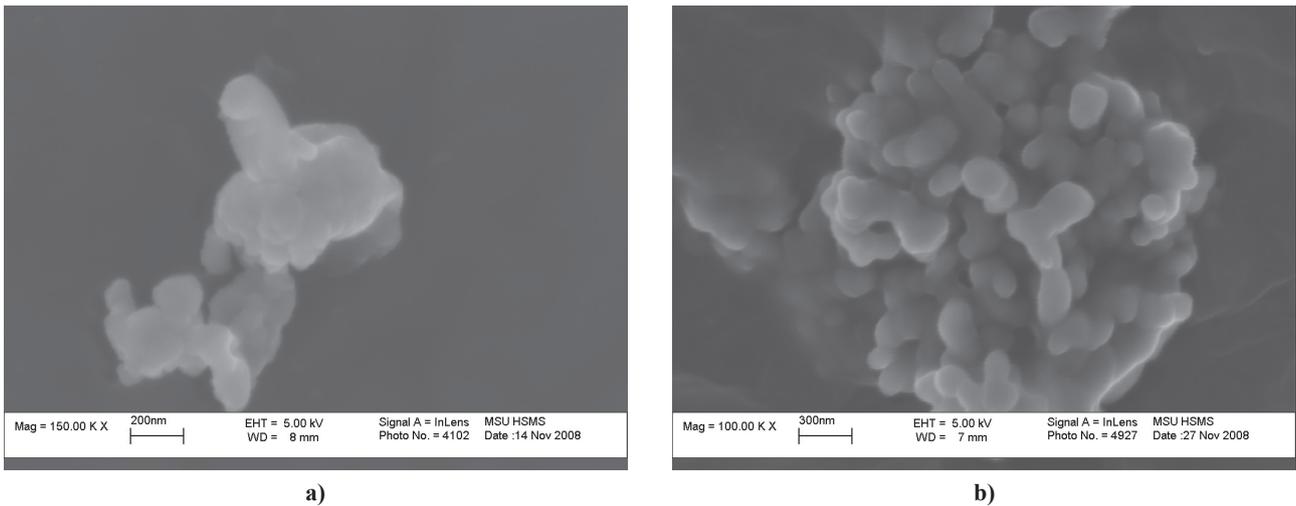


Figure 6. SEM micrographs of: a) as-synthesized AHCPP and b) powder after thermal treatment at 600 °C

Table 1. Density, average grain size and bending strength of the CPP ceramics

Temperature [°C]	Relative density [%TD]	Strength [MPa]	Average grain size [µm]
900	87	70	0.5 – 2
1000	79	50	10 – 30
1100	79	55	10 – 30

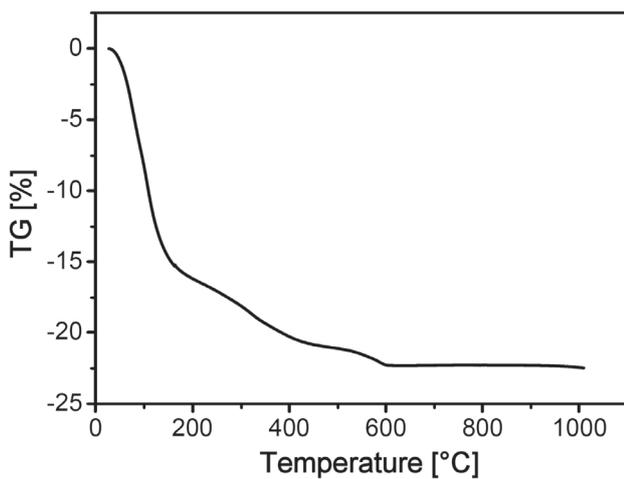


Figure 7. TGA of AHCPP powder

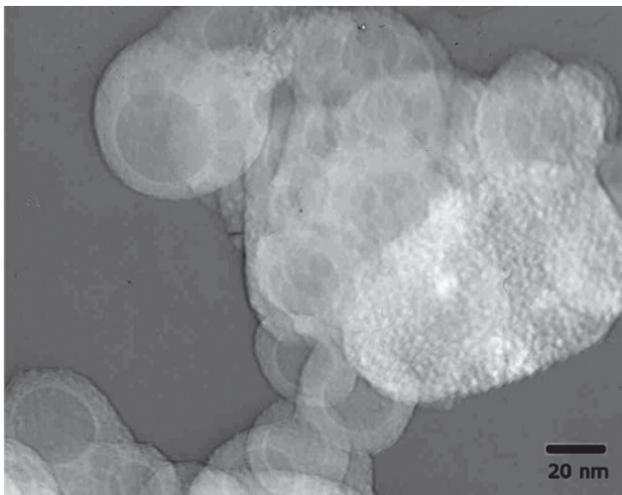


Figure 8. TEM micrograph of AHCPP powder

the processes mentioned above are completed at 600 °C. Further increase of the temperature is not desirable due to the intensive sintering and grain growth. Thus, the temperature of 600 °C was chosen as an optimum annealing temperature because it is high enough to allow complete decomposition and elimination of by-products as well as avoid significant sintering. X-ray diffraction patterns demonstrate the formation of the β- and α-phase CPP during thermal treatment. The formation of high-temperature metastable phases during the heat treatment was reported earlier [9] in the cases of amorphous calcium phosphate (ACP) and pyrophosphate (AHCPP). Their presence is likely connected to the structural similarity between the corresponding amorphous and high-temperature crystalline phases. TEM analysis shows that AHCPP particles acquire mesoporous structure with a wide pore size distribution (Fig. 8). It should be noted that this material was quite sensitive to the electron beam, a behaviour resembling ACP.

Finally, the method described above enables the production of pure calcium pyrophosphate powder with particles smaller than 200 nm that can be easily sintered at relatively low temperature.

Sintering at maximum temperatures of 900, 1000 and 1100 °C was done to investigate the sinterability of the pressed samples. Surprisingly, the relative density and strength of ceramic materials decrease significantly with the increase of sintering temperature (Table 1). This fact can be explained by the SEM images. In Fig. 9, abnormal grain growth is observed in the samples sintered at 1000 and 1100 °C. Abnormal grain growth can be ascribed to the formation of the melt at high temperatures. In the case

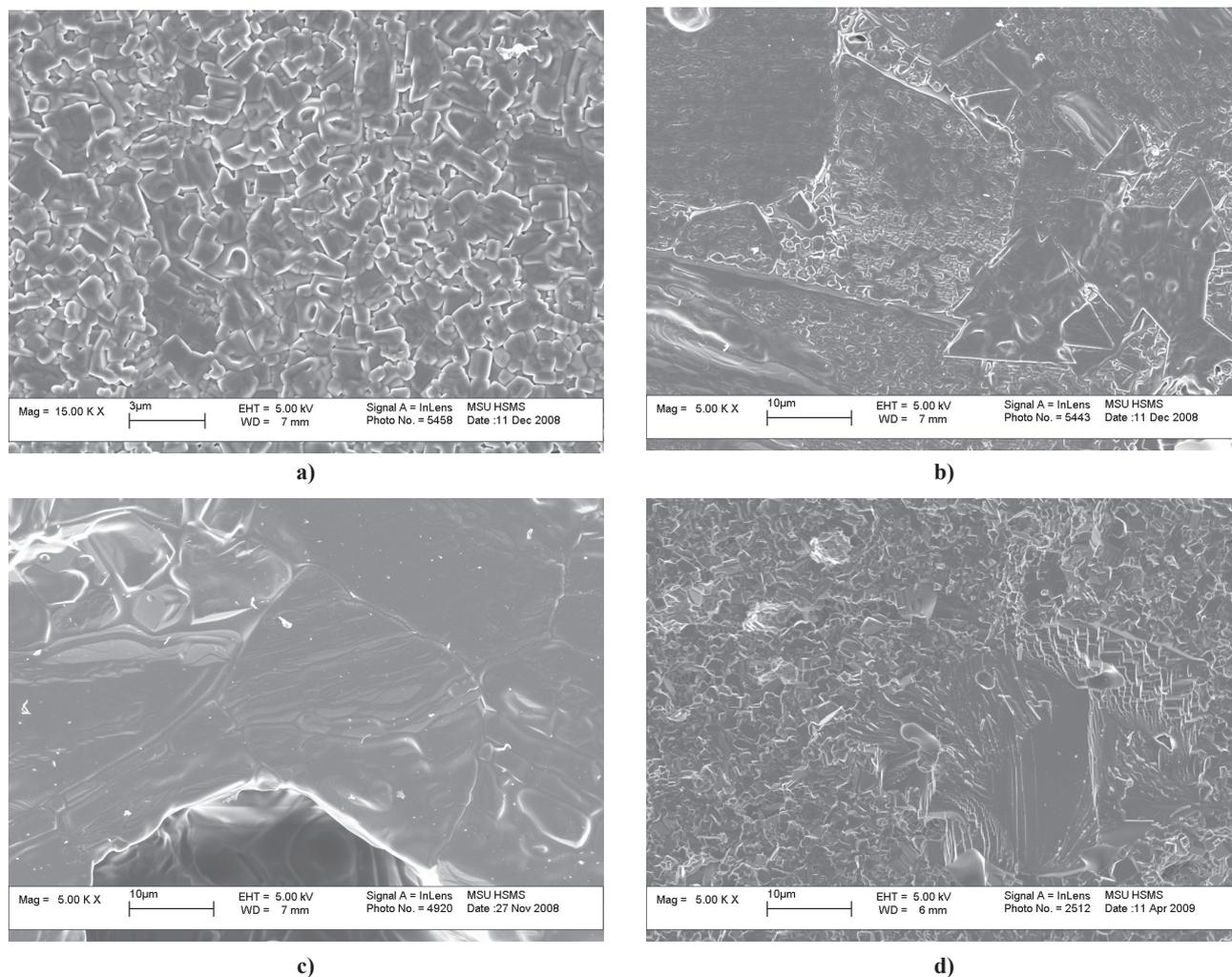


Figure 9. SEM micrographs of: a) ceramics sintered at 900 °C, b) ceramics sintered at 1000 °C, c) ceramics sintered at 1100 °C and d) surface of fracture after compressive test of ceramics sintered at 900 °C

of the sample sintered at 900 °C, the grains look significantly smaller (Fig. 9a) compared to those in the samples sintered at higher temperatures. Figure 9d shows that the cracks propagate through the grains, i.e. transgranular fracture of the ceramics occurs. Strong bonding between the grains is underlying such behaviour.

IV. Conclusions

It has been established that synthesis of amorphous calcium pyrophosphate by mixing ammonium pyrophosphate and calcium nitrate solutions and subsequent thermal treatment leads to the formation of calcium pyrophosphate powders with particle sizes below 200 nm. By starting with this amorphous hydrated calcium pyrophosphate powder as a precursor it is possible to obtain relatively dense (up to 87% TD) and strong fine-grained ceramics.

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