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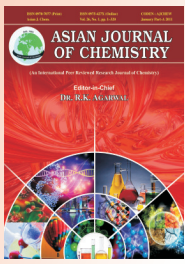

Synthesis of Barium Hydrogen Phosphate by Biomimetic Method in Beef Extract and Typtone Matrix

XIAONIU YU[1,2], CHUNXIANG QIAN[1,2,*] and XIN WANG[1,2]

[1]School of Materials Science and Engineering, Southeast University, Nanjing 211189, P.R. China
[2]Research Institute of Green Construction Materials, Southeast University, Nanjing 211189, P.R. China

*Corresponding author: E-mail: cxqian@seu.edu.cn

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Barium hydrogen phosphate precipitate was induced using organic templates. The structure, morphology, size and thermal properties of the precipitates were characterized by energy dispersive X-ray spectroscopy, X-ray techniques, scanning electron microscope, particle size analyzer, thermogravimetric-differential scanning calorimetry analysis. Particle size analyzer furnish evidence for the formation of $BaHPO_4$ with average crystallite size 11.99 and 30.47 μm. Thermogravimetric-differential scanning calorimetry curves showed that barium hydrogen phosphate precipitate induced in pure water was more thermal stability than one induced in organic templates. The results display that organic matrix play an important roles in the process of crystal nucleation, growth and accumulation of barium hydrogen phosphate.

Keywords: Barium hydrogen phosphate, X-ray techniques, Morphology, Particle size analyzer, Thermal properties.

INTRODUCTION

The formation of mineral phases in organic macromolecules is a key feature of natural biomineralization processes. Biominerals, natural inorganic/organic hybrid materials, are formed through a cooperative interaction of inorganic materials with organic macromolecules, where the macromolecules control the nucleation, growth, morphology, structure and crystal orientation of the inorganic component[1,2]. Moreover, biominerals with controlled structure are generally formed by self-organization and under mild solution conditions. Recently biomineralization has achieved much attention from biologists, chemists and material scientists[3-6]. In recent years, Organic matrix, which have been used as a new class of additives to control the morphology and size of inorganic crystals, such as Au[7], Ag_2S[8,9], $CaCO_3$[4,10], CdS[11], $BaHPO_4$[3], $LiFePO_4/C$[6], *etc*.

The alkaline earth phosphates, such as $MHPO_4$, have been extensively studied in the past years for their applications in different domains such as bioceramics, ionic conductivity, ferroelectrics, luminescence, metal-doping and corrosion resistance[12-15]. But there are a few papers about the shape and texture of barium hydrogen phosphate by mimicking the biomineral synthesis. In recent years, only Wang *et al.*[3] controlled the morphology of barium hydrogen phosphate by using organic templates, which gives different shapes at different pH values: hexagon, sphere cluster, sphere with rough surface, sphere with relatively smooth surface and small sphere. The results show that organic macromolecules is able to tailor the size and shape of synthesized particles, which has important influences on the morphology of products.

Here, we report the preparation and characterization of $BaHPO_4$ particles by biomineralization process. Results of this research provide a new route to synthesize special shapes and sizes materials.

EXPERIMENTAL

All raw materials were of analytically pure grade and used without further purification. Deionized water was self-made. XRD (Bruker Company, Germany) analysis was carried out on sample at room temperature by a D8-Discover X diffraction meter (40 kv, 40 mA) with Cu (λ = 1.5406 Å) irradiation at the rate of 0.15 s/step in the range of 10-90°. SEM (FEI Company, Netherlands, operating voltage 20 kV) with a genesis 60S energy dispersive X-ray spectroscopy (EDS) spectroscopy system was used to conduct morphological studies and to measure the elemental compositions of the samples. Particle size was determined using a microtrac S3500 particle size analyzer (Advanced Research Tools Corporation, Downers Grove, Illinois, USA) for dispersions of $BaHPO_4$ particles in pure water. Thermogravimetric-differential scanning calorimetry (DSC-TG) was carried out on STA449 F3 thermogravimetric analyzer (Netzsch, Germany). The analyses were carried out simultaneously in a nitrogen atmosphere at a heating rate of 10 °C/minute between room temperature and 700 °C.

Chemical precipitation of barium hydrogen phosphate (BHP) (BHP-1): Na_2HPO_4 (20 mM) was completely dissolved in a bottle with 200 mL water. $BaCl_2 \cdot 2H_2O$ (20 mM) was added to the above solution. The precipitates were allowed to stand under static conditions for 24 h at room temperature. As a result, BHP-1 was synthesized.

Biomineralization precipitation of barium hydrogen phosphate (BHP) (BHP-2): 0.6 g beef extract, 1 g typtone, 1 g NaCl were completely dissolved in 200 mL of deionized water and its pH value was adjusted to 7 using diluted NaOH solution. Next, 200 mL of mixture solution was added to 500 mL flask bottle and bottle was wrapped by employing gauze and paper. The bottle was placed in autoclave under 125 °C and 0.1 Mpa conditions for 25 min. After cooling above solution, 20 mM of Na_2HPO_4 was perfectly dissolved in the solution. As the same procedure mentioned in the "Chemical Method" section, the BHP-2 was also obtained.

RESULTS AND DISCUSSION

An elemental analysis of samples composition is performed using EDS to confirm the presence of elements O, P and Ba in the BHP-1 and BHP-2 samples (Fig. 1). The XRD of materials analysis further confirms that BHP-1 and BHP-2 patterns can be readily indexed to the reported structures of $BaHPO_4$ (JCPDS Card No. 72-1370) and no peaks attributable to impurities are observed (Fig. 2).

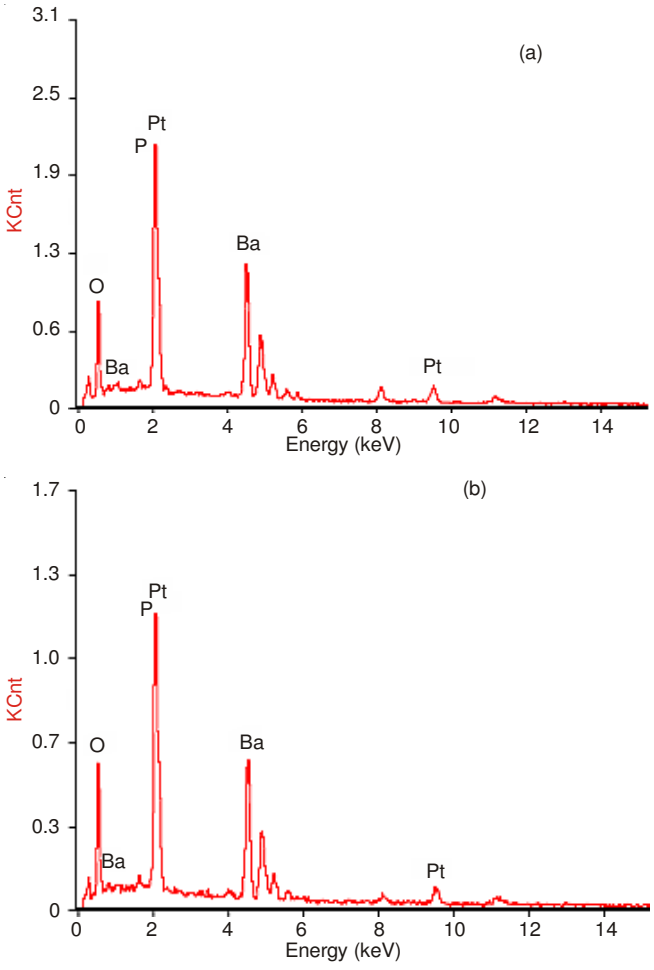

Fig. 1. EDS spectrum of barium hydrogen phosphate, (a) BHP-1, (b) BHP-2

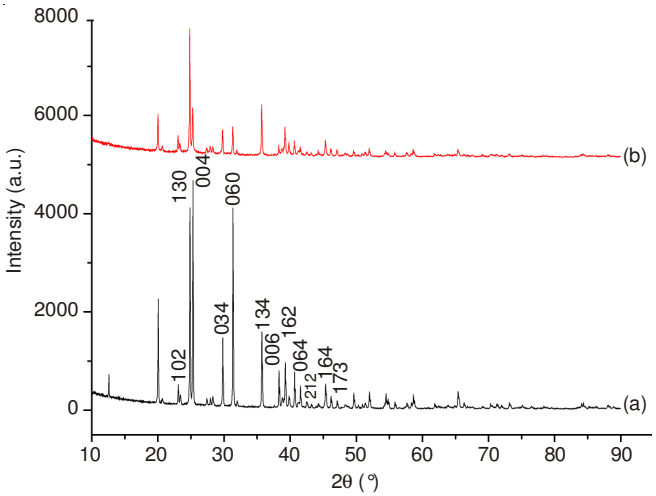

Fig. 2. XRD patterns of barium hydrogen phosphate, (a) BHP-1, (b) BHP-2

Scanning electron microscope (SEM) and particle size distribution images of barium hydrogen phosphate crystals that precipitated in the presence of water and organic matrix are shown in Figs. 3 and 4, respectively. Fig. 3 a and b show that the morphology of barium hydrogen phosphate-1 particles is the hexagonal shape with a rough surface is observed. The particles length and width are 3.89 to 26.16 μm (Fig. 4). Spheres accompany with some irregular sphere and spherical cluster appear, as shown in Fig. 3c and d. The size of the spheres, irregular spheres and spherical cluster is not uniform; the diameter ranges from 3.27 to 104.6 μm (Fig. 4). The wide diameter distribution may be caused by containing a small amount of spherical cluster by SEM micrographs. The above average crystallite size calculates by particle size distribution data, are found to be 11.99 and 30.47 μm. From the SEM images, it is observed that the crystal particles arrange from hexagonal shape, *via* spheres, to irregular shape to spherical cluster with not uniform size. The mechanism of the whole changing process remains unclear and needs further study.

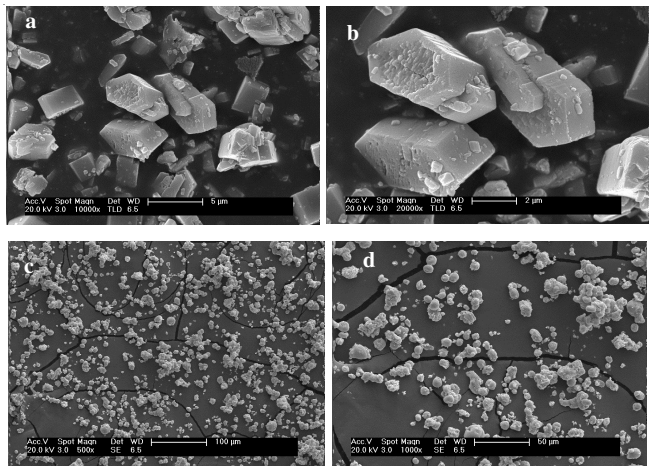

Fig. 3. SEM images of barium hydrogen phosphate obtained in the presence of water, beef extract and typtone, (a) BHP-1, (b) BHP-2

DSC-TG curves of BHP-1 and BHP-2 particles are displayed in figures Fig. 5. From the results, it is observed that DSC curves show endothermic peaks at 441.2 and 426.5 °C for BHP-1 and BHP-2 particles, respectively. These values

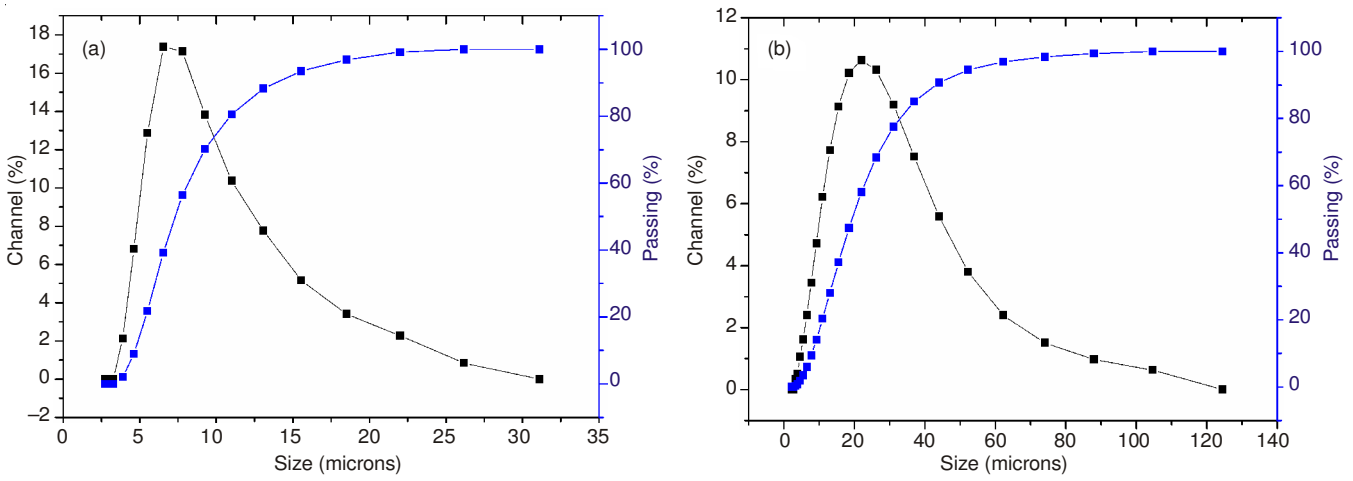

Fig. 4. Particle size distribution of barium hydrogen phosphate particles, (a) BHP-1, (b) BHP-2

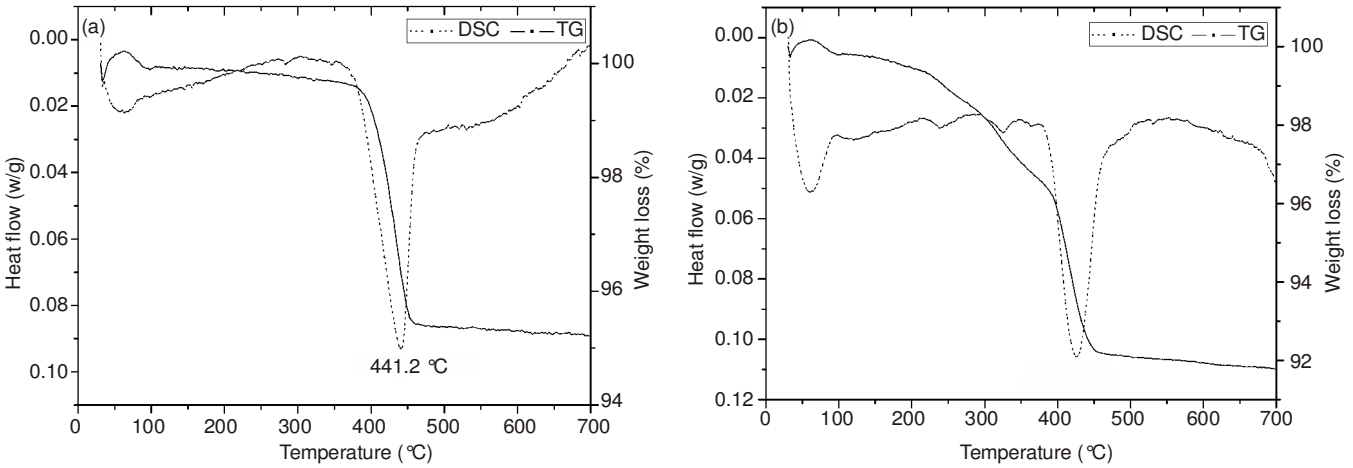

Fig. 5. DSC-TG curves of barium hydrogen phosphate particles, (a) BHP-1, (b) BHP-2

can be considered as the decomposition or melting points of the samples. From the results it is noticed that BHP-1 particles has more thermal stability than BHP-2 particles which may be due to decrease in bond energy caused by containing a small amount of organic matrix. The TG curves of BHP-1 and BHP-2 particles show that maximum weight loss occurs in the temperature range 400-455 °C which is due the decomposition of the samples.

Conclusion

The work shows that diverse shapes and size of the barium hydrogen phosphate particles can be obtained in the presence of yeast extract and peptone. We find that the shape of barium hydrogen phosphate appears irregular, from spheres, *via* irregular sphere to spherical cluster with diameter ranges from 3.27 to 104.6 μm. The barium hydrogen phosphate induced precipitate in organic matrix have more lower decomposition or melting points than one induced in pure water and it may be due to decrease in bond energy caused by containing a small amount of organic matrix.

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