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Simple and Rapid Synthesis of $Fe(PO_3)_3$ by Microwave Sintering

Weijia Zhou,[†] Wen He,*[,†,‡] Xudong Zhang,[†] Jianan Liu,[†] Yi Du,[†] Shunpu Yan,[†] Xiuyin Tian,[†] Xianan Sun,[†] Xiuxiu Han,[†] and Yuanzheng Yue[†,§]

Department of Materials Science and Engineering, Key Laboratory of Glass-Ceramics, Shandong Institute of Light Industry, Jinan 250353, People's Republic of China, Biomaterials Research Center, South China University of Technology, Guangzhou 510640, People's Republic of China, and Section of Chemistry, Aalborg University, DK-9000 Aalborg, Denmark

$Fe(PO_3)_3$ with different morphologies has been synthesized using H_3PO_4 and Fe_2O_3 as starting compounds by microwave sintering. The structure and morphologies of resultant samples were characterized by X-ray diffractometry, thermogravimetry/differential scanning calorimetry, Fourier transform infrared spectroscopy, and transmission electron microscopy. The $Fe(PO_3)_3$ crystals obtained from microwave sintering have high thermal stability and good micromorphology. The crystal transformation of $Fe(PO_3)_3$ and the synthesis mechanism are simply discussed.

1. Introduction

The solid-state chemistry of polyphosphates is traditionally considered unusual because the transition metal exhibits a trivalent oxidation state. These compounds have interesting properties such as magnetic, heterogeneous catalysis, ionic exchange, and optical.[1,2] The $Fe(PO_3)_3$ metaphosphate belongs to a series of polyphosphates with the general formula $M(PO_3)_3$ (M = Cr, Fe, Ti),[3−5] which are characterized by a tridimensional network of isolated MO_6 octahedra connected through PO_4 tetrahedra. In particular, $Fe(PO_3)_3$ exhibits an antiferromagnetic behavior below $T_N = 10$ K due to special structural features.[6]

$Fe(PO_3)_3$ is generally synthesized by solid-state methods. Thus, we began exploring a simple method to synthesize $Fe(PO_3)_3$ at low temperature. Microwave processing is a self-heating process through the absorption of electromagnetic energy. Compared with conventional methods, microwave synthesis has the advantages of rapid growth, small particle size, and low temperature. This processing has been applied in preparing many nanomaterials, such as $LiFePO_4$,[7] HAP,[8] ZnO,[9] and InP.[10]

In this paper, we present the crystal structure and morphological properties of $Fe(PO_3)_3$ obtained by microwave sintering. The synthesis mechanism of $Fe(PO_3)_3$ is simply discussed.

2. Experimental Section

2.1. Materials and Methods. The starting materials used in this study included ferric oxide (Fe_2O_3; 99.0 %, Tianjin Bodi Chemical Co., Ltd.) and phosphoric acid (H_3PO_4; 85.0 % by weight, Tianjin Bodi Chemical Co., Ltd.). Both chemical reagents were analytical grade.

The $Fe(PO_3)_3$ was synthesized using Fe_2O_3 and H_3PO_4 at different ratios ($R = C_P/C_{Fe}$), and 0.01 mol of Fe_2O_3 and different volumes of H_3PO_4 (R = 3, 3.5, and 4) were mixed and stirred adequately. The mixture of Fe_2O_3 and H_3PO_4 underreacted at ambient temperature. The precursor solution was heated in a microwave oven (Galanz, 800 W, 2145 GHz) at 600 W for different irradiation times until the reaction was complete. After instantaneous violent reaction, a spongy solid was obtained. Then the resulting spongy solid was ground. Finally, the resultant powders were washed sufficiently with distilled water and ethanol and dried at 80 °C for 6 h. For R = 3 and 3.5, some resultant powders were calcined at (350, 450, and 550) °C for 2 h. The samples uncalcined and calcined were used for further characterization.

2.2. Characterization. The X-ray diffraction (XRD) technique was performed on an X-ray diffractometer with Cu Kα ($\lambda = 0.15418$ nm) irradiation (D8-ADVANCE, Bruker AXS GmbH, Germany). The chemical bond linkages of the samples were studied by FT-IR spectroscopy (Tensor27, Bruker AXS GmbH, Germany) by a KBr wafer technique. Thermal analysis was carried out in N_2 by thermogravimetric analysis (TG) and differential scanning calorimetry (DSC) (TG/DSC; STA 449C, NETZSCH, Germany) at a heating rate of 10 °C·min^{-1}. The morphological features of samples were investigated with an electron microscope (JEM-2010, JEOL, Japan), using an accelerating voltage of 100 kV. Samples for TEM were prepared by air-drying a drop of sonicated ethanol suspension of powders onto a gelatin-coated copper mesh.

3. Results and Discussion

To define optimal experimental conditions, a series of investigations were undertaken. The reaction of Fe_2O_3 and H_3PO_4 depends on the R value, and the XRD results are shown in Figure 1. For R = 3, the precursors react incompletely and a broad amorphous hump is detected in Figure 1a. For R = 3.5, Fe_2O_3 and H_3PO_4 react thoroughly and a white spongy solid is obtained. All the reflection peaks in Figure 1b are the same as the standard values of $Fe(PO_3)_3$ crystals (JCPDS no. 44-0772). For R = 4, the positions of the peaks in Figure 1c are the same as those in Figure 1b. Therefore, the value of R = 3.5 should be suitable for synthesizing $Fe(PO_3)_3$ crystals.

The amorphous product obtained by microwave sintering for R = 3 was calcined at different temperatures of (350, 450, and 550) °C. The XRD pattern of the resultant samples is shown in Figure 2. When the sample is heated at 350 °C, the $FeH_3P_2O_6·3H_2O$ and $FeH_2P_2O_7$ phases appear as shown in

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* Corresponding author. E-mail: hewen1960@126.com. Phone: +86-0531-89631018. Fax: +86-0531-89631518.
[†] Shandong Institute of Light Industry.
[‡] South China University of Technology.
[§] Aalborg University.

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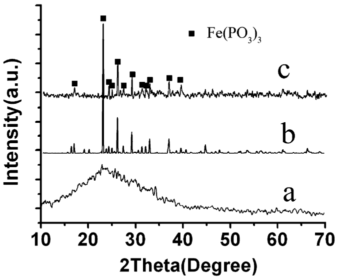

Figure 1. XRD pattern of microwave-synthesized $Fe(PO_3)_3$ at different R values: (a) 3, (b) 3.5, (c) 4.

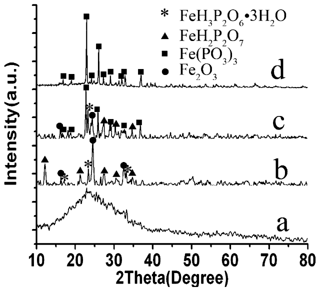

Figure 2. XRD pattern of microwave-synthesized hybrid iron phosphate for (a) $R = 3$ and calcined at (b) 350 °C, (c) 450 °C, and (d) 550 °C for 2 h.

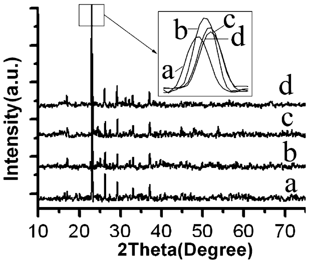

Figure 3. XRD pattern of microwave-synthesized $Fe(PO_3)_3$ for (a) $R = 3.5$ and calcined at (b) 350 °C, (c) 450 °C, and (d) 550 °C for 2 h.

Figure 2b. Some reflections for unreacted Fe_2O_3 are also apparent in Figure 2b. When the temperature reaches 450 °C, $FeH_3P_2O_6•3H_2O$ and $FeH_2P_2O_7$ have transformed into $Fe(PO_3)_3$. The $Fe(PO_3)_3$ phase is dominant in the product as shown in Figure 2c. When the sample is calcined at 550 °C, all impure phases transform into the pure $Fe(PO_3)_3$ phase and all diffraction peaks match with the standard $Fe(PO_3)_3$ peaks as shown in Figure 2d. The XRD pattern indicates pure $Fe(PO_3)_3$ crystals were obtained by structural transformation of other iron phosphate phases during calcination. The crystalline transformation process results are similar to previous results.[11]

The positions of the peaks for microwave-synthesized $Fe(PO_3)_3$ crystals ($R = 3.5$) with different heat treatment temperatures are identical as shown in Figure 3. The crystallinity of microwave-synthesized $Fe(PO_3)_3$ is specific and unaffected by temperature. The peak intensity of $Fe(PO_3)_3$ remains basically invariant with increasing temperature from 80 to 550 °C, and the changes of the peak position can be neglected (Figure 3, inset). Therefore, heat treatment is not necessary for the well-crystallized $Fe(PO_3)_3$ obtained by microwave sintering for $R = 3.5$.

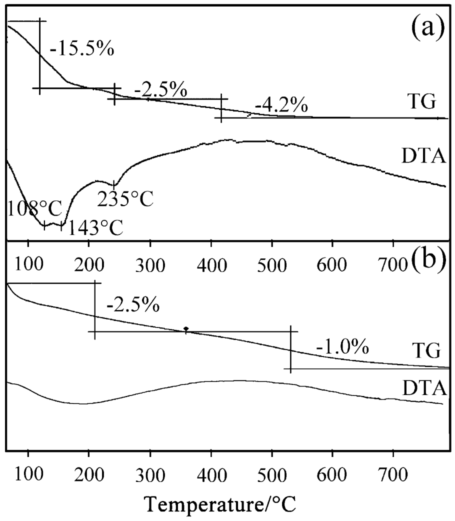

Figure 4. TG/DSC of the microwave-synthesized $Fe(PO_3)_3$ samples for (a) $R = 3$ and (b) $R = 3.5$.

Figure 4 shows simultaneous TG and DSC plots of microwave-prepared $Fe(PO_3)_3$ samples with different R values. In Figure 4a, the DSC curve of the sample with $R = 3$ has endothermic peaks around (108, 143, and 235) °C. The endothermic peaks at (108 and 143) °C with a corresponding TG peak of -15.5 % are related to the loss of moisture and dehydration. An endothermic peak was observed around 235 °C, which indicates the reaction of residual H_3PO_4 and Fe_2O_3. The TG curve shows a weight loss of -2.5 % at the corresponding temperature due to the loss of water obtained from the reaction of H_3PO_4 and Fe_2O_3. The broad exothermic hump over a wide temperature range is observed, indicating the crystallization and crystal transformation processes are very complex and slow. The corresponding weight loss is only -4.2 %. In Figure 4b, the DSC curve of the sample with $R = 3.5$ does not exhibit obvious endothermic and exothermic peaks. The corresponding weight loss from (100 to 800) °C is only -3.05 %, indicating the stable thermal properties of resultant $Fe(PO_3)_3$ crystals. The DSC and TG result is consistent with the XRD result (Figures 2 and 3).

The reaction mechanism of microwave-synthesized $Fe(PO_3)_3$ was investigated. The variation of the reaction time for $R = 3$ at different microwave powers of (500, 600, 700, and 800) W is (5, 3, 2, and 2) min, respectively. The reaction time is mainly used to consume free water. When free water disappears, the reaction occurs immediately. To investigate the microwave absorbent which provides energy for the reaction, comparative experiments were carried out. One microwave-synthesized amorphous iron phosphate sample (S1, $R = 3$) was mixed with water, and consequently, a suspending liquid was formed. The other sample (S2, $R = 3$) was laid aside in an air environment for enough time to adsorb planar water and formed a soft solid. The two samples were put into a microwave oven at 600 W for 5 min. The result is that S2 reacted severely and S1 was unreacted. According to the above results, the microwave absorbent is not water but phosphoric acid. In the S2 sample, the unreacted metaphosphoric acid transforms into phosphoric acid by adsorbing planar water. The dehydration process restarts to provide energy for the reaction of metaphosphoric acid and ferric oxide. In the S1 sample, the free water hinders the dehydration process of phosphoric acid.

On the basis of the XRD and above results, a reaction mode is proposed. The basic reaction process is as follows: (a) When free water is completely consumed, phosphoric acid as a microwave absorbent dehydrates 1 mol of water and transforms into metaphosphoric acid. The reaction can be written as follows:

$$H_3PO_4 \rightleftarrows HPO_3 + H_2O \qquad (1)$$

(b) At the same time, the dehydration process provides energy for the following reaction. The metaphosphoric acid reacts with

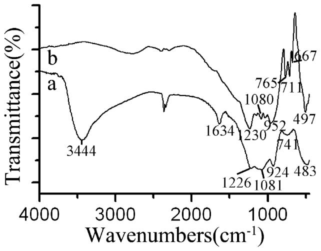

Figure 5. FT-IR spectra of as-synthesized $Fe(PO_3)_3$ by calcining at 550 °C for (a) $R = 3$ and microwave heating for (b) $R = 3.5$.

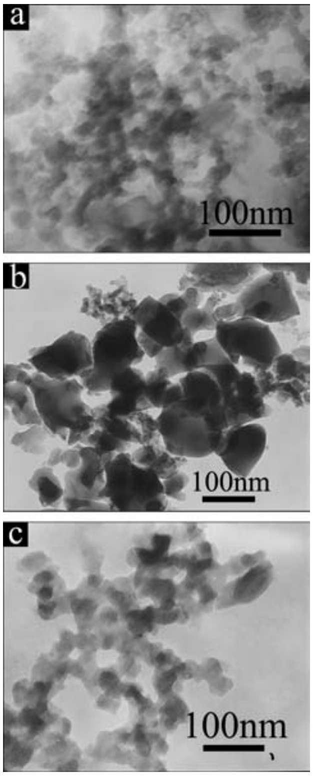

Figure 6. TEM images of microwave-synthesized iron metaphosphate: (a) $R = 3$, (b) $R = 3.5$, (c) $R = 4$. The sample with $R = 3$ was calcined at 550 °C for 2 h.

ferric oxide to form $Fe(PO_3)_3$. The reaction can be written as follows:

$$6HPO_3 + Fe_2O_3 \rightleftarrows 2Fe(PO_3)_3 + 3H_2O \qquad (2)$$

According to Figure 2 and the chemical equations, the reactive ratio for $R = 3$ should be sufficient for the reaction. However, the reaction is incomplete. The possible reasons are undermixing or deficient energy obtained from insufficient H_3PO_4. For $R = 3.5$, Fe_2O_3 and H_3PO_4 completely react due to superfluous H_3PO_4. Therefore, the nonsymmetric vibrations of O−H groups in H_3PO_4 as a microwave absorbent provide energy for the reaction of Fe_2O_3 and H_3PO_4.

The main bands in the IR spectrum of $Fe(PO_3)_3$ obtained in different ways are shown in Figure 5. In curve a, the peaks at (3444 and 1634) cm^{-1} serve as an identity of adsorbed water. The strong bands at (1226 and 924) cm^{-1} are assigned to stretching antisymmetric vibration of the P−O group, and the peak at 741 cm^{-1} is ascribed to the symmetric stretching of the P−O group. The broad band at 1081 cm^{-1} is due to the simultaneous existence of PO_2 and PO_3 groups in $Fe(PO_3)_3$. The band at 483 cm^{-1} is ascribed to the antisymmetric stretching of the Fe−O group. In curve b, the characteristic peaks of adsorbed water disappear due to the residual HPO_3 in the $Fe(PO_3)_3$ sample. The characteristic peaks of $Fe(PO_3)_3$ obtained by microwave sintering for $R = 3.5$ at (1230, 1080, 952, 765, 711, 667, and 497) cm^{-1} are similar with those of $Fe(PO_3)_3$ obtained by conventional calcining. Comparing parts a and b of Figure 5, the splitting peaks at (765, 711, and 667) cm^{-1} (curve b) obtained from the peak at 741 cm^{-1} (curve a) are due to high crystallinity with better atomic order.[12]

Figure 6 shows the morphologies of iron metaphosphate obtained in different conditions. The TEM image in Figure 6a shows that the resultant iron metaphosphate ($R = 3$) calcined at 550 °C has approximately disk shapes with a mean diameter of (20 to 30) nm. The flaky iron metaphosphate nanoparticles sinter together due to the high temperature. The lamellar morphology is dominant in the product synthesized by microwave heating for $R = 3.5$ (Figure 6b). The novel gossamer-like thin layers have an irregular shape and a porous surface. The morphology of $Fe(PO_3)_3$ for $R = 4$ is shown in Figure 6c, and the macroporous framework structure composed of $Fe(PO_3)_3$ nanoparticles is observed. According to the TEM results, the microwave sintering is beneficial to form the fine morphologies of $Fe(PO_3)_3$ with different R values.

4. Conclusions

The purpose of this study was to investigate a simple and rapid synthesis method to synthesize $Fe(PO_3)_3$ using H_3PO_4 and Fe_2O_3 as starting materials. For $R = 3.5$, the synthesis of nanosized $Fe(PO_3)_3$ with a thin layer morphology was carried out by microwave sintering, and well-crystallized $Fe(PO_3)_3$ powders were obtained. It was demonstrated that H_3PO_4 as a microwave absorbent promotes the reaction of H_3PO_4 and Fe_2O_3. The microwave sintering is a promising method for fast synthesis of nanometer materials. Advantages of the technique in this study are listed as follows: (a) The method is a simple and economical synthesis process. (b) $Fe(PO_3)_3$ is well-crystallized without high-temperature treatment. (c) The novel nanostructure is obtained without any surfactants. (d) The reaction process produces no byproduct. Moreover, the technique presented here is a promising way for the preparation of various other $M(PO_3)_3$ (M = Cr, Fe, Ti) nanomaterials.

Acknowledgment

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