

Microwave-Assisted Hydrothermal Synthesis of Zinc Phosphates of Varying Dimensionality

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Abstract: By applying microwave-assisted heating approach, a one-dimensional (1D) chained zinc phosphate structure, $Zn(C_3N_2H_4)HPO_4$ (Compound I), and a two-dimensional (2D) layered zinc phosphate, $Zn_4P_3O_{11}(OH) \cdot 3C_3N_2H_4$ (Compound II), have been obtained in the $Zn(OAc)_2$ - H_3PO_4 -Imidazole- H_2O hydrothermal reaction system. Their structures were determined by single-crystal X-ray diffraction and further characterized by powder XRD and SEM analysis. The results indicate that the compounds composed of the same construction units possess different structures and dimensions. One-dimensional zinc phosphate (Compound I) is easily obtained when the crystallization temperature is low or the reaction time is short. Under the premise of constant raw material ratio of the precursor solution, two-dimensional zinc phosphate (Compound II) can be obtained by increasing the crystallization temperature or prolonging the reaction time. In addition, the transformation of compound I to II can be achieved by adjusting the reaction temperature and reaction time.

Key words: microwave; hydrothermal synthesis; crystal structure; zinc phosphate; phase transition

微波水热法合成不同维数磷酸锌化合物的研究

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摘要: 利用微波辅助水热合成的方法, 在醋酸锌-磷酸-咪唑-水体系中获得了一维链状磷酸锌, $Zn(C_3N_2H_4)HPO_4$ (化合物 I) 和二维层状磷酸锌, $Zn_4P_3O_{11}(OH) \cdot 3C_3N_2H_4$ (化合物 II)。通过单晶 X 射线衍射分析确定其结构, 并利用粉末 XRD 和 SEM 对产物进行了进一步的研究。结果表明, 两种不同结构、不同维数的化合物, 具有相同的构筑单元。当晶化温度较低或反应时间较短时, 易得到一维磷酸锌(化合物 I); 在前驱体溶液的原料配比不变的前提下, 提升晶化温度或延长反应时间会得到二维磷酸锌(化合物 II)。此外, 通过控制反应温度和反应时间可以实现化合物 I 到化合物 II 的转变。

关键词: 微波合成; 水热合成; 晶体结构; 磷酸锌; 相转变

1 Introduction

Since Stucky et al.^[1] synthesized microporous zinc phosphates with zeolite like topologies for the first time, a variety of zinc phosphates with open frameworks of different dimensionalities, including one-dimensional (1D) chained struc-

tures^[2-6], two-dimensional (2D) layered structures^[5, 7-10] and a large number of three-dimensional (3D) open framework structures^[5, 11, 12], have been synthesized and characterized. Generally these compounds were synthesized by hydrothermal/solvothermal methods in the presence of organic amines.

Microwave-assisted hydrothermal synthesis has been widely employed in many recent chemical reaction studies owing to its rapid heating, homogeneity, and higher yield^[13-17]. In a previous study, open-framework zinc phosphates were synthesized by microwave-assisted technique, and the morphologies of the products can be controlled by changing the synthesis conditions^[18].

In this study, 1D chained structure, $Zn(C_3N_2H_4)HPO_4$

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(Compound I), and 2D layered structure, $Zn_4P_3O_{11}(OH) \cdot 3C_3N_2H_4$ (Compound II), were obtained in the same reaction system under microwave heating. Pure compound II has been successfully synthesized by using conventional hydrothermal method^[5, 9]. The reaction conditions of compound I and II were investigated in detail, and the structures of the two zinc phosphate compounds were analyzed.

2 Experimental Section

A typical experiment was as follows: 1.23 g zinc acetate and 1.15 g imidazole were added into 7 ml deionized water,

and stirred to form a transparent solution. Then 0.385 ml phosphoric acid was added drop by drop with vigorous stirring and a white precipitation formed. The molar composition of the mixture was 1.0($Zn(OAc)_2$) : 1.0(H_3PO_4) : 3.0(Imidazole) : 70.0(H_2O). The mixture was stirred for 1 h, then transferred into a 70 ml Teflon autoclave for microwave radiation heating under the reaction temperature for 30 min. After reaction, the solid products were washed with deionized water and dried at room temperature. The complete synthesis conditions and compositions of the products obtained by powder XRD analysis are presented in Table 1.

Table 1 Synthesis conditions and analysis for compounds

No.	Gel composition (molar ratio) $Zn(OAc)_2 : H_3PO_4 : Imidazole : H_2O$	$T/^\circ C$	t/min	Product	XRD pattern (Fig. 2)	SEM image (Fig. 3)
1	1 : 1 : 3 : 70	140	30	I	2a (c)	-
2	1 : 1 : 3 : 70	160	30	I	2a (d)	(a)
3	1 : 1 : 3 : 70	170	30	I + II	2a (e)	(b)
4	1 : 1 : 3 : 70	180	30	I + II	2a (f)	(c)
5	1 : 1 : 3 : 70	190	30	I + II	2a (g)	(d)
6	1 : 1 : 3 : 70	200	30	II	2a (h)	(e)
7	1 : 1 : 3 : 70	180	15	I	2b (a)	(f)
8	1 : 1 : 3 : 70	180	20	I + II	2b (b)	(g)
9	1 : 1 : 3 : 70	180	90	II	2b (d)	(h)
10	1 : 1 : 3 : 70	180	180	II	2b (e)	-
11	1 : 1 : 3 : 50	180	30	I + II	2c (a)	(i)
12	1 : 1 : 3 : 100	180	30	II	2c (c)	(j)
13	1 : 1 : 3 : 140	180	30	II	2c (d)	-

Powder XRD data were collected on a XRD-6100 diffractometer, which offers the scan rate of $5 (^\circ)/min$, with $CuK\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at room temperature. The scanning electron microscopy (SEM) images were taken on a JSM-6460LV electron microscope operating at 15 kV. The structures of the products were analyzed by single-crystal diffraction, and the intensity data were collected on a Siemens diffractometer fitted Bruker SMART CCD detector using graphite-monochromated $Mo-K_\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$).

3 Results and Discussion

The framework structures of compound I and compound II were showed in Fig. 1.

The structure of compound I consists of ladders, which are formed by strictly alternating corner-sharing ZnO_3N and $PO_3(OH)$ tetrahedra. The imidazole molecule is connected to the Zn center via the Zn-N bond and located between the ladders. The structure of compound II is built up from the vertex-shared PO_4 , $PO_3(OH)$, ZnO_4 , ZnO_2N_2 and ZnO_3N tetrahedra. The imidazole molecule acts not only as a structure-di-

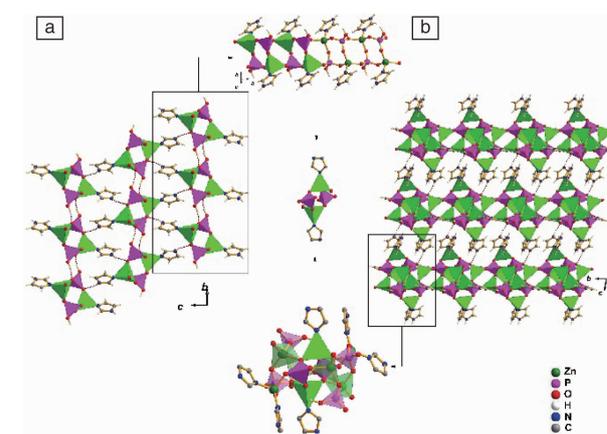


Fig. 1 Polyhedral representation of framework structures along the a -direction: (a) compound I, (b) compound II

recting agent but also as a ligand to Zn. Different from compound II, the structure of compound I does not consist of any Zn-O-Zn linkage. From Fig. 1, it can be seen that the 4-membered ring is the basic structural building unit in these two zinc phosphate compounds. The effect of crystallization tem-

perature was studied by varying the temperature from 140 °C to 200 °C. Powder XRD and SEM were used to monitor the evolution of the products as the crystallization temperature increased (Fig. 2a and Fig. 3a ~ 3e). It can be seen that pure compound I was generated when the temperature was 140 °C or 160 °C. However, the yield of product at 140 °C was lower than that in 160 °C. When the crystallization temperature was raised up to 170 °C, the powder XRD pattern shows a reflection peak of compound II ($2\theta \approx 7.4^\circ$). As shown in SEM images, the external surfaces of crystals became rough (Fig. 3b). The XRD pattern at 180 °C exhibits presence of both compound I and II. The morphology of the products is irregular and the crystal size of both compound I and II became smaller. When the reaction mixture was heated at 200 °C, pure compound II was obtained. The resulting crystals were aggregated and their sizes became larger and narrower.

Fig. 2b and Fig. 3c, Fig. 3f ~ 3h show the XRD patterns and SEM images of the zinc phosphates synthesized at 180 °C with different crystallization time. Pure compound I was formed after the mixture was heated for 15 min. The presence of compound II was observed when the crystallization time was increased to 20 min. The resulting crystals became larger obviously, but their morphology was poor. As the crystallization went on, the intensity of characteristic peaks of compound II increased, while those of compound I decreased. When the reaction time was extended to 90 min, pure compound II was observed. The morphology of which is regular and uniform. The crystallinity of the product decreased slightly when the crystallization time was extended to 180 min. The transformation from compound I to II indicates that compound II is more stable than compound I. The reason might be there are much more Zn-N bonds in compound II than in compound I.

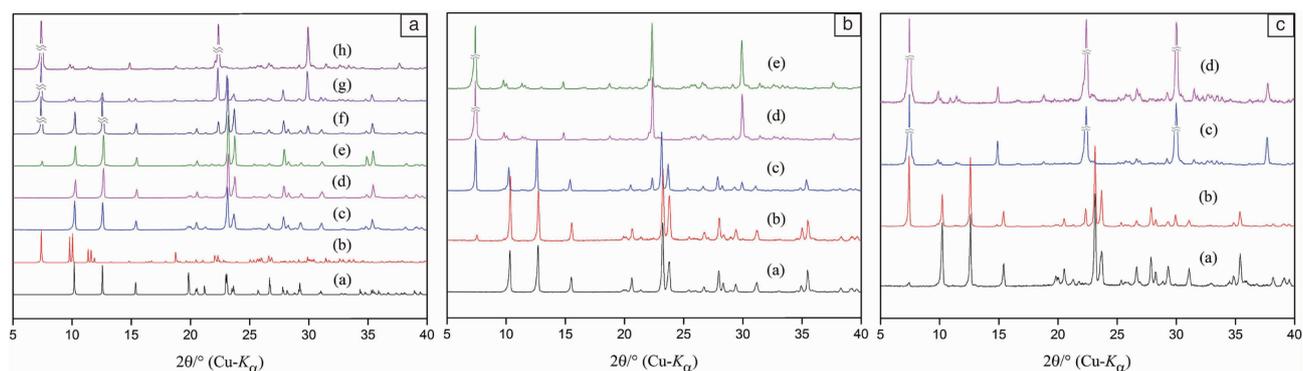


Fig. 2 XRD patterns of products with different reaction conditions: (a) different crystallization temperature, (b) different crystallization time and (c) different $\text{H}_2\text{O}/\text{Zn}(\text{OAc})_2$ molar ratios

The syntheses of zinc phosphates with $\text{H}_2\text{O}/\text{Zn}(\text{OAc})_2$ molar ratios of 50, 70, 100 and 140 were conducted under similar conditions, respectively. The XRD patterns and SEM images of the products with different amounts of H_2O are shown in Fig. 2c and Fig. 3c, Fig. 3i, Fig. 3j, respectively. When the $\text{H}_2\text{O}/\text{Zn}(\text{OAc})_2$ molar ratio was 50, Compound I was obtained. However, the product was not pure, and the

morphology of which was large and rough (Fig. 3i). Two compounds coexisted when the $\text{H}_2\text{O}/\text{Zn}(\text{OAc})_2$ molar ratio increased to 70. Pure compound II was obtained when the ratio increased to 100. Increasing this ratio to 140, the products did not change much. The pH value of the reaction mixture, which is affected by the content of H_2O , might influence which products were formed.

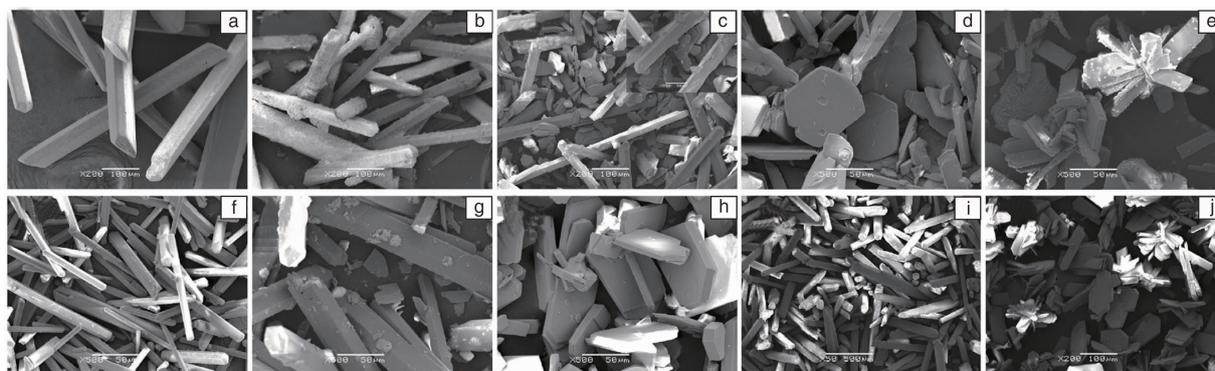


Fig. 3 SEM images of products synthesized under different crystallization conditions

4 Conclusion

In this study, 1D chained zinc phosphate compound I and 2D layered compound II were synthesized successfully by microwave-assisted heating in the same reaction system. The reaction conditions have been investigated in detail and found that increasing the microwave radiation temperature or prolonging the reaction time, compound II was obtained easily. Changing the content of H₂O would affect the pH of the precursor solution, as well as the dimensionality of the resulting structures. We also found that the 4-membered ring is the basic structural building unit in the two structures of different dimensionalities, and believe the structures of compound I and II have some unknown relationships, which will be investigated further. Compared to conventional hydrothermal synthesis method, microwave heating method shows greater superiority which promoted the growth of crystals, lowered crystallization temperature and reduced crystallization time, thus saving energy.

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