

Preparation of $\text{Na}_{1+x}\text{Fe}_4\text{P}_{12}$ Whiskers by Hydrothermal Reduction Alloying Synthesis Method

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Skutterudite $\text{Na}_{1+x}\text{Fe}_4\text{P}_{12}$ whiskers were prepared by a new hydrothermal reduction alloying method. The diameter of the whisker is about 0.5–4 μm and its L/D ratio is about 10–20. Heating temperature and time can control the diameter and length of the skutterudite whisker. X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscope (TEM), electronic diffraction (ED), and X-ray fluorescence analysis have been employed to characterize the products. XRD and ED revealed that the whiskers obtained at 200 °C are cubic skutterudite with $a = 7.7995 \text{ \AA}$. X-ray fluorescence analysis proved that there are sodium atoms in the skutterudite structure. The possible formation mechanism of $\text{Na}_{1+x}\text{Fe}_4\text{P}_{12}$ is proposed.

Introduction

FeP_3 is one of several compounds with the CoAs_3 or skutterudite structure. This family of compounds has recently been identified as prospective candidates for good thermoelectric materials.^{1,2} In addition to their potential applications, skutterudites are a fascinating compound family. The skutterudite family consists of compounds of the form of AB_3 , where A is Co, Ir, Fe, or Rh and B is As, P, or Sb. The crystal structure, as shown in Figure 1, is characterized by the formation of four-member pnictide rings that are located in the center of the cubes formed by the metal atoms.^{3,4} For every four metal cubes, there is one void, without the four-member pnictide ring. This void can be filled with different atoms such as La or Ce to obtain the related compound family called filled skutterudites. The filled skutterudites have excellent thermoelectric properties and are called electron crystals and phonon glasses.^{5,6}

Although the filled skutterudite $\text{LaFe}_4\text{P}_{12}$ has been synthesized by a flux synthesis technology by Jeitschko and Braun,⁷ to our knowledge, no study on alkaline-filled FeP_3 skutterudite has been published because it

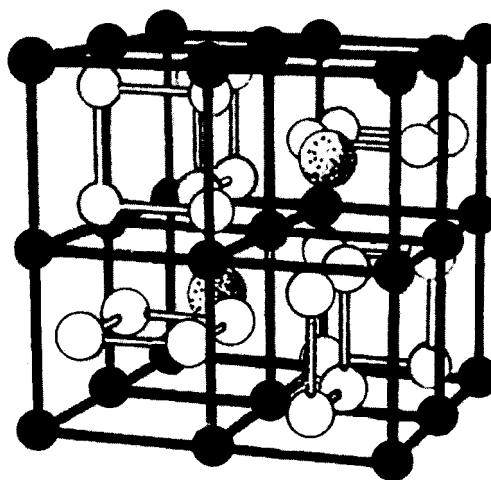


Figure 1. Skutterudite structure of AB_3 (A is Co, Ir, Fe, or Rh; B is As, P, or Sb) The black ball represents A atom, and the white ball represents B atom.

is difficult to synthesize by the conventional synthesis method. In this paper, a hydrothermal synthesis method for preparation of the crystalline $\text{Na}_{1+x}\text{Fe}_4\text{P}_{12}$ is reported. It is very interesting that the morphology of $\text{Na}_{1+x}\text{Fe}_4\text{P}_{12}$ is a rodlike crystal, which is a typical whisker. This synthesis involves hot NaOH reacting with white phosphorus to form hydrogen phosphide, then hydrogen phosphide reduces $\text{Fe}(\text{OH})_3$ to iron, and finally FeP_3 is formed from iron and phosphorus from the decomposition of hydrogen phosphide.

Experimental Section

For preparing FeP_3 , about 0.6 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 1 g of NaOH, and 1 g of white phosphorus were added to 12 mL of distilled water in a stainless steel autoclave with a Teflon liner of 16

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Table 1. Treatment Settings To Synthesize Skutterudite $\text{Na}_{1+x}\text{Fe}_4\text{P}_{12}$ Whiskers

setting	$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (g)	NaOH (g)	white phosphorus (g)	heating temp ($^\circ\text{C}$)	heating time (h)
1	0.6	1	1	200	15
2	0.6	1	1	200	24
3	0.6	1	1	200	40
4	0.6	1	1	210	24
5	0.6	1	1	220	24
6	0.6	1	1	230	24
7	0.6	1	1	240	24
8	0.2	1	1	200	24
9	0.6	1	1	200	24
10	1.0	1	1	200	24
11	1.2	1	1	200	24

mL capacity. The autoclave was heated according to different treatment settings (Table 1) to investigate the effect of the heating temperature and time on the composition and morphology of the product. Some other reaction conditions (also

see Table 1) were set to investigate the effect of the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /white phosphorus ratio in the reactant on compositions of the products. The products obtained were washed by HCl (pH = 1–2) and distilled water, then washed by CS_2 to eliminate the excess phosphorus, and dried at 60°C in a vacuum drier.

The final gray product powders were characterized by XRD on a D max- γ A model (Japan Rigaku) X-ray diffraction with Ni-filtered Cu $K\alpha$ radiation. The scanning electron microscopy (SEM) and the transmission electron microscope (TEM) observations as well as the electronic diffraction experiments were carried out on a Hitachi model H-800.

Results and Discussion

The pH values of all the product solutions heated according to the above setting are 2–3. In such a solution, there is no $\text{Fe}(\text{OH})_3$.

The left hand panels of Figure 2 show the XRD patterns of the product powders obtained at different

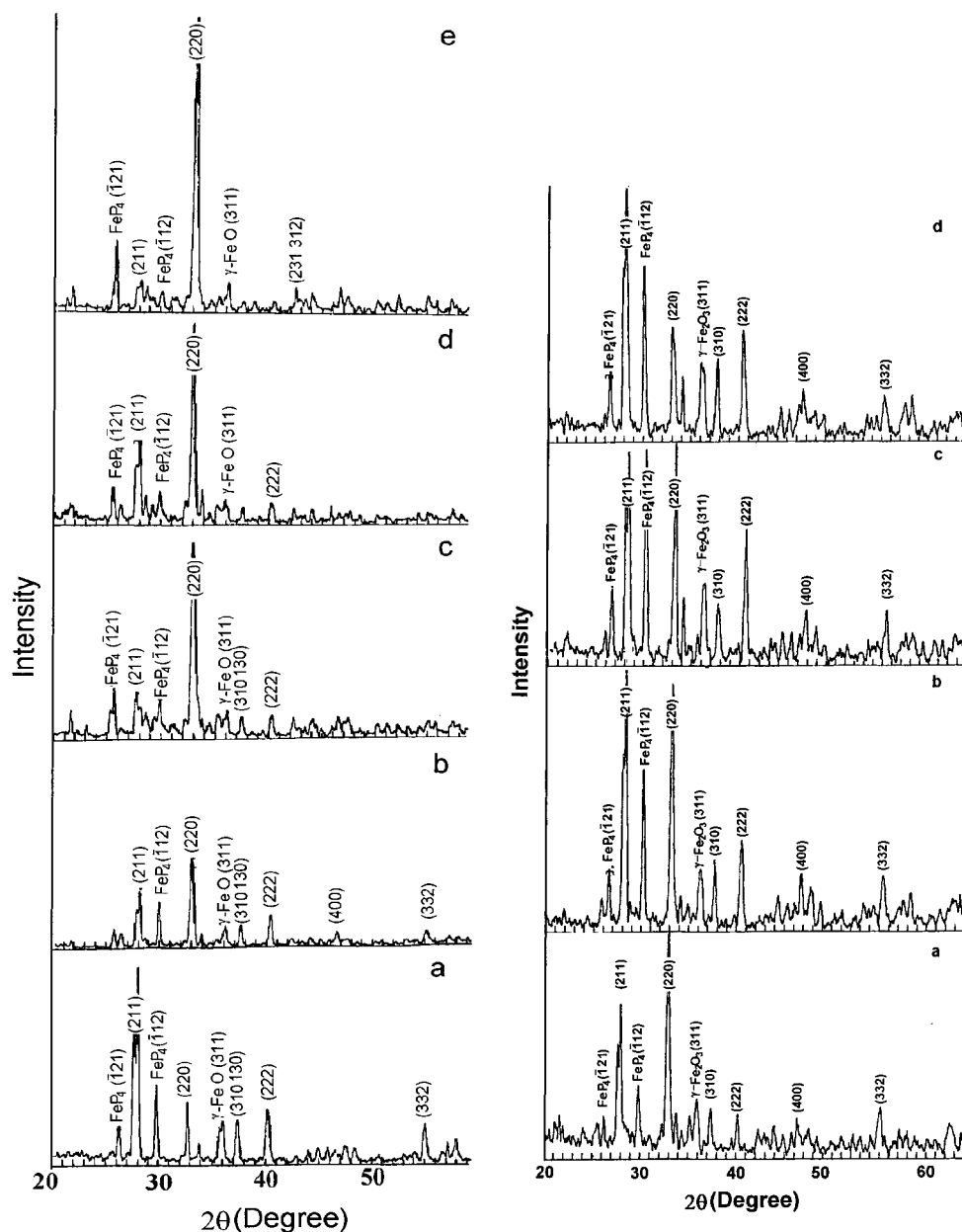


Figure 2. XRD patterns of the samples. (Left-hand panels) XRD patterns of the products obtained at different temperatures for 24 h: (a) 200°C , (b) 210°C , (c) 220°C , (d) 230°C , and (e) 240°C . (Right-hand panels) XRD patterns of the product for different $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /white phosphorus ratios obtained at 200°C for 24 h.

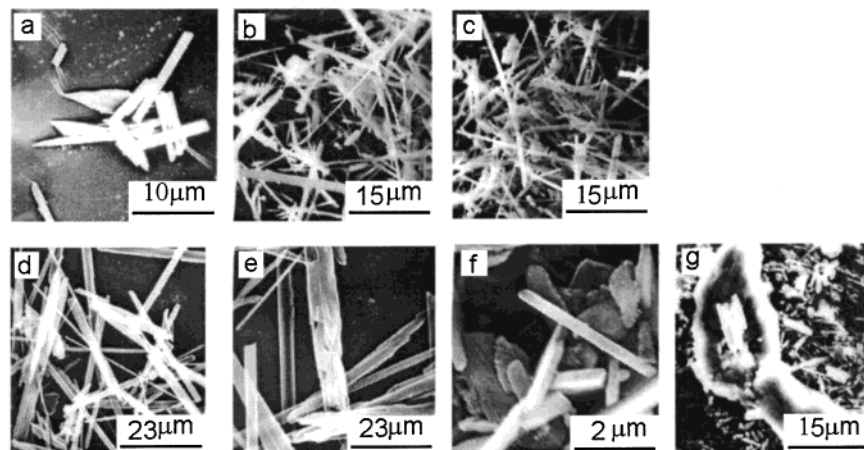


Figure 3. SEM images of the product powders (a) obtained at 200 °C for 15 h, (b) obtained at 200 °C for 24 h, (c) obtained at 200 °C for 40 h, (d) obtained at 220 °C for 24 h, and (e) obtained at 240 °C for 24 h. (f) Plate particles in the product; (g) spongelike particles in the product.

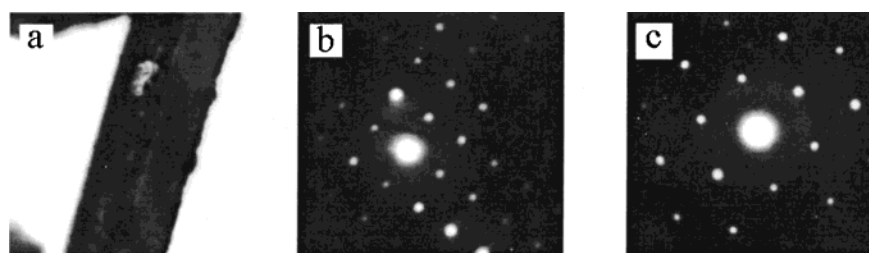


Figure 4. TEM and ED images of the skutterudite whisker obtained at 200 °C for 24 h. (a) TEM image; (b) ED image paralleling the [001] direction; (c) ED image paralleling the [111] direction.

temperatures (200, 210, 220, 230, and 240 °C) for 24 h. Many peaks of the patterns correspond to the skutterudite-type $\text{LaFe}_4\text{P}_{12}$ synthesized by Jeitskcho and Braun.⁷ Beside the skutterudite, there is $\gamma\text{-Fe}_2\text{O}_3$ and FeP_4 (JCPD25–1402, JCPD34–995) in all of the product powders. Iron hydroxyl and iron phosphate, as well as other iron–phosphorus compounds (FeP or FeP_2), do not appear in the product. From the patterns, we find that the relative intensity of the (211) peak of the skutterudite decreases and that of the (220) peak increases with increased heating temperature. The variation of the intensity of the peaks is related to the shape of the skutterudite crystalline particles formed from the reaction. Perhaps the skutterudite crystal grows along a special direction. The relative intensity of the peak of Fe_2O_3 decreases with increased heating temperature. Therefore, we can deduce that the content of Fe_2O_3 in the product powder decreases with increased heating temperature. From Figure 2 (left), we can also see the (121) peak of FeP_4 increases and the (112) peak decreases with increased heating temperature. This effect is also caused by the directional growth of FeP_4 particle in the synthesis.

The right-hand panels of Figure 2 show the XRD patterns of the product powders obtained at 200 °C for 24 h at different $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /phosphorus ratios (0.2/1, 0.6/1, 1.0/1, and 1.2/1) in the reactant. When the ratio is very low (0.2/1), the product powder mainly consists of skutterudite and a small amount of Fe_2O_3 and FeP_4 . The content of Fe_2O_3 and FeP_4 in the product increases with increasing $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ /phosphorus ratio.

The main phase structure of the powders can be identified as skutterudite with cubic structure by analyzing the XRD pattern. The cell parameter of skut-

terudite obtained at different temperatures calculated from the XRD pattern is $a = 7.768\text{--}7.803 \text{ \AA}$, which is smaller than that of the filled skutterudite $\text{LaFe}_4\text{P}_{12}$ ($a = 7.832 \text{ \AA}$)⁷ and close to that of cerium-, samarium-, praseodymium-, and neodymium-filled skutterudite, $\text{Ce}(\text{Sm}, \text{Pr}, \text{Nd})\text{Fe}_4\text{P}_{12}$ ($a = 7.79\text{--}7.81 \text{ \AA}$).⁸

Figure 3 shows the SEM images of the products obtained from different settings. All of the products obtained at 200–240 °C mainly consist of whiskers. The product powders obtained at 200 °C for different temperatures are whiskers 0.5–1.5 μm in diameter. From the figures, it is observed that whiskers formed at the same temperature have the same diameter. The length of the whiskers increases with increased heating time, from 10 μm for 15 h to 40 μm for 40 h. Whiskers obtained at 220 °C are 1–3 μm in diameter, and those obtained at 240 °C are 2–4 μm in diameter. We can conclude that the diameter of the whiskers increases with the heating temperature, and the length of it increases with increased heating time at the same temperature.

Figure 4 shows the transmission electron microscopy (TEM) image and the electron diffraction (ED) images of a whisker obtained at 200 °C for 24 h. The ED image shows the whisker is a single crystal with cubic structure, where panels b and c are the diffraction patterns paralleling the [001] and [111] directions of the crystal, respectively. The cell parameter of the crystal calculated from the patterns is $a = 7.8 \text{ \AA}$, which is closed to the lattice parameter calculated from the diffraction pattern.

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Table 2. Element Composition of the Products Synthesized at 200 and 220 °C for 24 h

conditions	Fe (mass %)	P (mass %)	Na (mass %)
200 °C, 24 h	56.68	38.89	2.60
220 °C, 24 h	55.96	40.02	3.51

Besides the rodlike particles, there are plate particles (Figure 3f) and spongelike particles (Figure 3g) in all of the product powders. X-ray energy spectra dispersion analysis shows that the rodlike and plate particles are Fe–P compounds and the spongelike particle mainly consists of iron (the elements oxygen and hydrogen cannot be detected). Therefore, we deemed that the rodlike particle is skutterudite, the spongelike particle is γ -Fe₃O₄, and the plate particle perhaps is FeP₄.

The element analysis for the products was performed on an ARL-XRF X-ray fluorescence analyzer. The results are listed in Table 2. The content of phosphorus increases with increased heating temperature. For all three product powders, the ratio of Fe/P is larger than that calculated from the composition formula of FeP₃. It is caused by the existence of γ -Fe₂O₃ in the product.

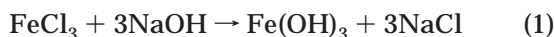
From Table 2, we find a certain amount of sodium element in all the product powders. As mentioned above, the products were washed by HCl and distilled water. All the free Na anions must be dissolved and removed during the washing procedure. Therefore, the sodium atoms can only exist in the cell lattice as filling atoms. From the composition formula of fully filled skutterudite NaFe₄P₁₂, the ratio of Na/P should be 1/12. The actual ratios of Na/P in the product powders obtained at 200 and 220 °C for 24 h are near and larger than the theoretical value, respectively. Perhaps two sodium atoms can occupy one void in some voids of skutterudite, because the sodium atom is much smaller than the void it occupies.

From Table 2, we can also find that the iron content in the product decreases with increased heating temperature, which agrees with the result of XRD.

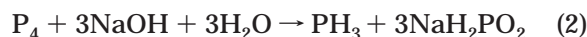
From all the characterizing experiments, we can confirm that the whisker in the products is fully or overly filled skutterudite Na_{1+x}Fe₄P₁₂.

Wang et al.⁹ have discovered a similar reaction during the reaction of NaOH with NiCl₂·6H₂O and white phosphorus. They found that the excess P could cause the formation of NiP₂, which was difficult to remove from the product. From the above discussion, we suggest the mechanism of forming filled skutterudite Na_{1+x}Fe₄P₁₂ as follows:

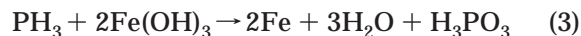
When all of the reagents are added to the distilled water in the autoclave, the following chemical process occurs and amorphous Fe(OH)₃ forms:



At high temperature, the white phosphorus reacts with the hot NaOH and the disproportionation of white phosphorus takes place:¹⁰



With its powerful reducibility, the PH₃ can reduce the Fe(OH)₃ formed at high temperature to iron, as it reduces the Ni(OH)₂:⁹



At the same time, thermal decomposition of PH₃ occurs at high temperature:¹⁰



As reported by Herms et al.,¹¹ phosphorus vapor consist of P₄ and a small amount of P₂ molecules. Because both the iron atoms and the gaseous phosphorus molecules, resulting from reducing reactions 3 and 4, respectively, are active and the phosphorus is excessive, the following alloying reaction should be carried out at high pressure:



Because the concentration of sodium cation is very high in the reaction solution, perhaps it can enter the void of the skutterudite FeP₃ to form filled skutterudite Na_{1+x}Fe₄P₁₂, when the alloying reaction is proceeding.

At the same time, the P₂ molecules can be combined with iron atoms and form FeP₄:



Because the content of P₂ in the phosphorus vapor increases with increasing temperature,¹¹ the content of FeP₄ in the product increases with increasing temperature. The increased FeP₄ content in the product with increased heating temperature detected by XRD can be explained by reaction 6.

The remnant iron hydroxyl spongelike precipitate that has not been reduced to iron can convert to γ -Fe₂O₃ at high temperature, which can be detected by XRD.

Conclusion

Na_{1+x}Fe₄P₁₂ whiskers with L/D ratio 10–20 are prepared by a new hydrothermal reduction alloying method. The heating temperature and time can control the diameter and length of Na_{1+x}Fe₄P₁₂ crystal. XRD patterns and ED pattern indicate that the cubic Na_{1+x}Fe₄P₁₂ with $a = 7.768\text{--}7.803$ Å is formed from the solutions at 200–240 °C. At the same time, FeP₄ plates and spongelike γ -Fe₂O₃ particles are formed. The content of γ -Fe₂O₃ and FeP₄ increases with increased heating temperature and the FeCl₃·6H₂O/white phosphorus ratio in the reactant. The Na_{1+x}Fe₄P₁₂ is obtained from the alloying reaction of iron reduced from Fe(OH)₃ by hydrogen phosphide and phosphorus from decomposition of the hydrogen phosphide. Hydrogen phosphide is produced from disproportionation of white phosphorus.

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