Pergamon

Materials Research Bulletin 37 (2002) 1101–1105

Materials Research Bulletin

A solvothermal synthesis of ultra-fine iron phosphide

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(Refereed)
Received 17 January 2002; accepted 7 March 2002

Abstract

Powder iron phosphide (FeP) has been prepared via a benzene-thermal synthesis with the reaction of anhydrous iron chloride ($FeCl_3$) and sodium phosphide (Na_3P) at 180–190°C. The product was analyzed by X-ray photoelectron spectroscopy (XPS), and the results show the mole ratio of Fe:P is 1.12. X-ray diffraction (XRD) pattern can be indexed to the orthorhombic cell of FeP with the lattice constant $a = 5.191$, $b = 3.101$, and $c = 5.789$ Å. Transmission electron microscope (TEM) images indicate that average particle size is about 200 nm in diameter.

Keywords: A. Inorganic compounds; B. Chemical synthesis; C. X-ray diffraction

1. Introduction

Iron phosphides, low-band gap semiconductors, are technologically important for luminescent devices and electronic components [1]. They have traditionally been prepared by a variety of thermal methods [2,3], among these include the direct high-temperature reaction of iron with red phosphorus under anaerobic conditions, the electrolytic reduction of iron oxides in the presence of alkali metal phosphates, and the high-temperature reaction of the metal or corresponding organometallic precursors with phosphines. Recently, iron phosphide was prepared by sonochemical synthesis from organometallic precursors after the amorphous material had been heated above 950°C and then slowly cooled to induce crystallization [4]. As the solvothermal synthetic technique has been developed as an effective and facile

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0025-5408/02/$ – see front matter
PII: S0025-5408(02)00749-3

measure for preparing cobalt phosphides [5], dinickel phosphide [6] and tin phosphide [7], herein we use this technique to synthesize crystalline iron phosphide (FeP) with the reaction of anhydrous iron chloride ($FeCl_3$) and sodium phosphide (Na_3P) at 180–190°C.

2. Experimental

In preparing the black precipitate Na_3P, analytically pure yellow phosphorus was washed free of water with absolute ethanol and benzene respectively, and the sodium were free of kerosene by washing with benzene. Appropriate amounts of the yellow phosphorus, sodium, and benzene was sealed in a Teflon-lined autoclave, and then heated at 150°C for 5 h and cooled to ambient temperature naturally. In a typical synthesis of FeP, appropriate amount of analytically pure iron chloride anhydrous ($FeCl_3$) and fresh benzene were sealed in the same autoclave immediately after the solution of the former reaction step was drawn off carefully. Again the autoclave was heated at 180–190°C for 24 h. After the autoclave was cooled to ambient temperature naturally, the obtained mixture was washed several times with acetone, distilled water, and absolute ethanol, respectively, to remove sodium chloride. The final product was dried in vacuum at 60°C for 4 h.

The gray powder product was analyzed by X-ray photoelectron spectroscopy (XPS) using an ESCAlab MK2 using Mg Kα radiation, powder X-ray diffraction (XRD) on an X-ray diffractometer (Rigaku rA) using Cu Kα radiation (wavelength $\gamma = 1.54178$ Å), and transmission electron microscope (TEM) with a Hitachi 800 TEM.

3. Results and discussion

XPS analyses of the as-prepared FeP sample are shown in Fig. 1. The survey spectrum (Fig. 1A) shows that the sample surface consists of phosphorus and iron. The oxygen may come from surface adsorption and oxidation of epidermal iron. Carbon was also found, which may be due to carbonization of solvent benzene in a small quantity, and carbon dioxide adsorption. The mole ratio of Fe:P is 1:1.12 (Fig. 1B–C), which is close to that of FeP.

The XRD pattern (Fig. 2) shows strong peaks of the crystalline iron phosphide. All the 17 peaks, at the *d*-spacing of 3.8502, 2.8993, 2.7377, 2.5989, 2.5293, 2.4207, 1.9901, 1.9605, 1.9306, 1.8831, 1.8095, 1.6567, 1.6383, 1.5495, 1.2980, 1.2708, and 1.2095 Å, can be indexed to the orthorhombic cell of FeP phase ((1 0 1), (0 0 2), (0 1 1), (2 0 0), (1 0 2), (1 1 1), (2 1 0), (1 1 2), (2 0 2), (2 1 1), (1 0 3), (3 0 1), (0 1 3), (0 2 0), (4 0 0), (1 1 4), and (2 2 2). The rms error of fit is 2.279E−04.), space group Pnma (No. 62), with the lattice constant $a = 5.191$, $b = 3.101$ and $c = 5.789$ Å, in good agreement with the reported value [8–10].

The TEM images of the sample (Fig. 3) show the as-prepared FeP powder exhibits complex morphology. The typical unshapely particles were from elliptical to

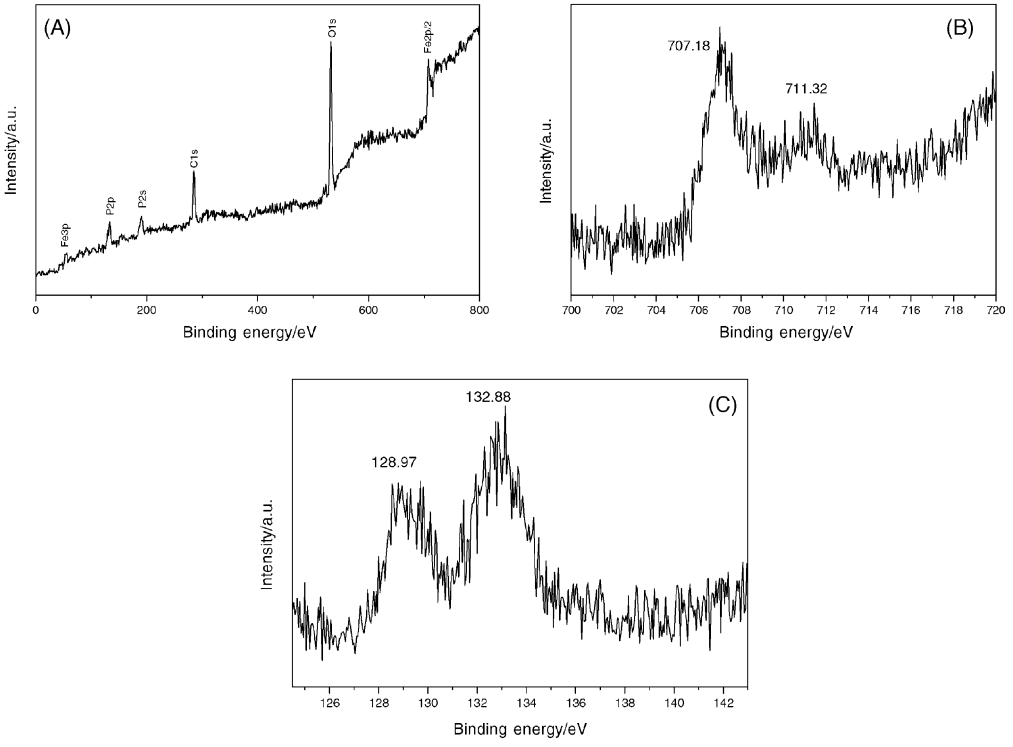

Fig. 1. XPS analyses of the as-prepared FeP sample. (A) Survey, (B) Fe region, and (C) P region.

spherical, and the particle size was non-uniform. The average particle size was estimated to be about 200 nm in diameter. Small amounts of scrappier and finer matter were also found clinging to and dispersing between the FeP grains. It may be amorphous carbon or iron oxides.

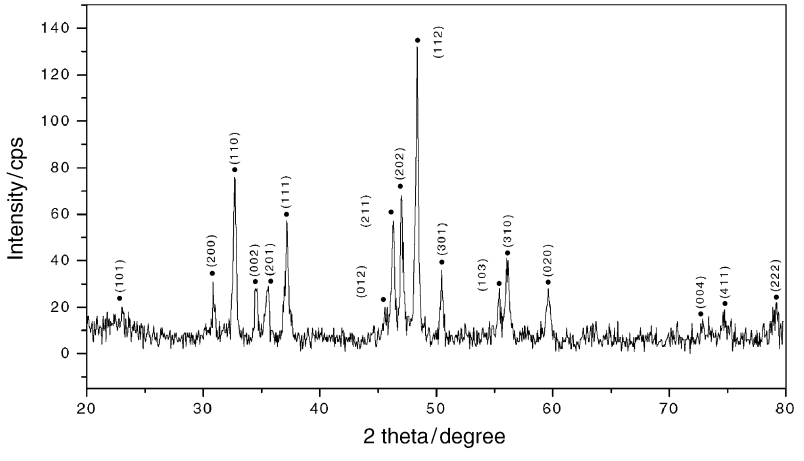

Fig. 2. XRD pattern of the as-prepared FeP sample.

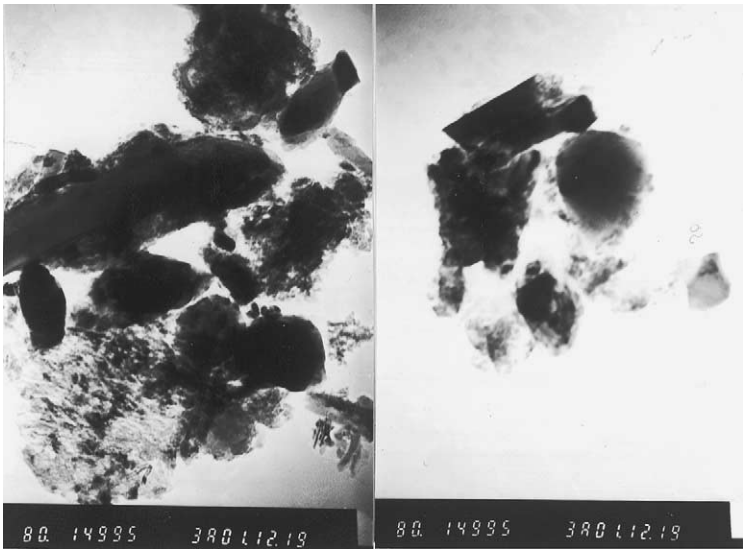

Fig. 3. TEM images of the as-prepared FeP sample (scale bar, 250 nm).

The benzene-thermal synthesis of crystalline FeP with the reaction of anhydrous iron chloride ($FeCl_3$) and sodium phosphide (Na_3P) can be described as follows:

$$FeCl_3 + Na_3P = FeP + 3NaCl$$

It may be a solid–liquid reaction, because anhydrous iron chloride is soluble in the benzene solvent. This technique depends on several factors, such as reaction temperature, time, and solvents selected. Benzene was chosen due to its superior solvency, as well as its appropriate boiling point. However, improvements are still needed in the solvothermal synthesis of crystalline FeP, such as discovering better solvents and optimizing reaction conditions.

4. Conclusion

In summary, ultra-fine iron phosphide (FeP) of the orthorhombic phase was successfully prepared via a benzene-thermal synthetic route by the reaction of anhydrous iron chloride ($FeCl_3$) and sodium phosphide (Na_3P) at 180–190°C. Our work verifies that the solvothermal synthesis technique is an effective and facile method for preparing metal phosphide.

Acknowledgments

Financial support from the Chinese National Foundation of Natural Science Research is gratefully acknowledged.

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