Solvothermal synthesis and magnetic properties of $\beta$-Co$_2$P nanorods

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Hexagonal high temperature phase $\beta$-Co$_2$P nanorods with a diameter of around 50 nm were synthesized via a mild solvothermal route. The reaction was carried out at 180 °C using cobalt chloride hexahydrate (CoCl$_2$·6H$_2$O) as Co source and yellow phosphorous as P source. The composition, structure as well as morphology were characterized by X-ray diffraction (XRD), X-ray photoemission spectroscopy (XPS) and transmission electron microscopy (TEM). The magnetic susceptibility curve indicates that the $\beta$-Co$_2$P nanorods show canted antiferromagnetic state, different from the paramagnetic state of orthorhombic low temperature phase $\beta$-Co$_2$P.

Keywords: solvothermal synthesis; magnetic materials; intermetallic alloys and compounds; nanocrystalline materials

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1. Introduction

Transition metals form a great class of metal phosphide compounds comprise over 125 binary and over 80 ternary substances because of the differences in metal characteristics and metal/phosphorus stoichiometry [1]. Many of them play a key role due to their potential applications in many fields, such as luminescent devices and electronic components [2], ferromagnetic materials and as superior catalysts [3]. According to the binary phase diagram of Co–P, two cobalt-containing phosphides, Co$_2$Si-type Co$_2$P and MnP-type CoP, are widely known at normal temperature and pressure [4]. Not incorporated in the phase diagrams are the polyphosphides CoP$_2$ and CoP$_3$, with CoSb$_3$-type and CoAs$_3$-type structures, respectively [5]. Since orthorhombic Co$_2$P is not stable up to the melting point at 1659 K [6], it is designated as the low temperature phase $\beta$-Co$_2$P, which has applications in catalysis of hydrodenitration [7]. In the temperature range of 1428 to 1659 K, another high temperature phase, designated as $\beta$-Co$_2$P, exists. This high temperature phase $\beta$-Co$_2$P is isotypic with Fe$_2$P and has a hexagonal structure [6]. As hexagonal $\beta$-Co$_2$P is only stable at high temperature, it is rather a challenge for us to realize the transformation of these two kinds of phase in considerable low temperatures and investigate their physical properties, as well.

Conventional synthesis of metal phosphides usually involves direct reaction of appropriate elements for prolonged periods at high temperature [8], reaction of phosphine with metals or metal oxides, reduction of metal phosphates by carbon, electrolysis of molten metal phosphate salts [9], metal organic chemical vapor deposition and the high-temperature self-propagating route [10–12]. These procedures typically require high reaction temperatures and long annealing periods to produce crystalline materials. Recently, C. M. Lukehart and his coworkers have reported a low temperature reaction, which creates crystalline nano-clusters of transition metal phosphides in a silica xerogel matrix by the decomposition of molecular precursors [13]. Furthermore, solution chemical synthesis techniques, such as solvothermal method, have also been developed for achieving
nanocrystalline $\beta$-Co$_2$P, Ni$_2$P and Fe$_2$P particles under rather mild temperatures [14–18]. Among these techniques, solvothermal method promises a single step of low-temperature metastable synthesis with superior composition and morphological control. In this paper, we present a facile solvothermal method, in which high temperature phase $\beta$-Co$_2$P nanorods can be successfully prepared. The magnetic behavior of this high-temperature stable phase shows a canted antiferromagnetic coupling interaction, while the orthorhombic low temperature phase $\beta$-Co$_2$P exhibits a common paramagnetic state.

2. Experimental

In the synthesis of $\beta$-Co$_2$P nanocrystals, CoCl$_2$·6H$_2$O and analytically pure yellow phosphorus were used as the starting materials with the molar ratio of 1:5. The typical synthesis procedure was as follows. An appropriate amount of yellow phosphorus, washed free of water using absolute ethanol and toluene successively, and CoCl$_2$·6H$_2$O were put into a 100 mL autoclave with Teflon liner, which was then filled with ethylenediamine up to 85% of its capacity. The autoclave was maintained at reaction temperature ($T_r$) of 180 to 240 °C for 24 to 72 h and then cooled to room temperature naturally. The black precipitate was collected and washed with benzene, distilled water, and absolute ethanol for several times in sequence. The final product was dried in vacuum at 80 °C for 12 h. The obtained products were characterized by D/max-2000 rotating powder diffractometer (Rigaku, Japan) using CuK$_\alpha$ radiation ($\lambda = 1.5406 \text{ Å}$). X-ray diffraction (XRD) patterns were obtained at a scanning rate of 8°/min over the 2θ range of 20° to 80°. Moreover, the morphology and size were both examined by transmission electron microscopy (TEM, Hitachi, H-800, Japan). Magnetization measurements were performed on a MagLab System 2000 (Oxford, UK) in the temperature range of 300 to 2 K.

3. Results and discussion

As-prepared Co$_2$P nanorods were structurally characterized by X-ray diffraction and shown in Fig. 1. All of the peaks are well indexed to hexagonal phase $\beta$-Co$_2$P, isotypic of Fe$_2$P [6]. When the reaction temperature of solvothermal synthesis decreased to 140 °C, orthorhombic $\beta$-Co$_2$P nanocrystallite has been produced, as well, which is coincident with the previous work by Xie et al. [14]. The natural preferential growth in the solvothermal system can be confirmed by the nanorod morphologies recorded by transmission electron microscopy (TEM, Hitachi, H-800, Japan) as shown in Fig. 2. The sample observed in Fig. 2a, was prepared at 180 °C for 48 h, and the fine nanorods aggregated seriously. In the meantime, we also observed that some small particles dispersed around the nanorods. Based on the electron diffraction results on these small particles, we found that the particles were amorphous. However, when $T_r$ rised up to 220 °C and the reaction time was prolonged to 72 h, some small nanorods dissolved and others grew bigger as observed in Fig. 2b. The average length of $\beta$-Co$_2$P nanorods prepared at 220 °C is about 1 µm with the diameter of 50 nm. In this solvothermal process, the possible reaction in the formation of cobalt phosphide can be described as follows [14]:

\[
P_4 + 14(\text{en}) + 16\text{H}_2\text{O} \rightarrow 14(\text{H}_2\text{en})^{2+} + 4\text{HPO}_4^{2-} + 20\text{e}^- \tag{1}
\]

\[
\text{Co}^{2+} + 6(\text{en}) \rightarrow \text{Co(en)}_6^{2+} \tag{2}
\]

\[
\text{Co(en)}_6^{2+} + 2\text{e} \rightarrow \text{Co} + 6(\text{en}) \tag{3}
\]

\[
8\text{Co} + P_4 \rightarrow 4\text{Co}_2\text{P} \tag{4}
\]

Trentler et al. [19] proposed a solution-liquid-solid (SLS) mechanism for the growth of III – V semiconductor fibers in organic solution, which could also explain the formation of $\beta$-Co$_2$P nanorods in our case. In this mechanism, the effective nucleation and growth is a critical factor for the synthesis of products with different morphologies. Hexagonal $\beta$-Co$_2$P is an anisotropic material with a unique

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c-axis, and nanorods usually can be obtained under the condition of fast growth rate by raising the reaction temperature. Moreover, during the process of this reaction, the intermediate formation of ferromagnetic metal Co accelerated the aggregation of subsequently created sample because of ferromagnetic coupling.

Fig. 1. XRD pattern of a $\beta$-Co$_2$P nanorod at 220 °C.

To examine the composition and purity of $\beta$-Co$_2$P nanorods, the as-prepared samples were studied by X-ray photoelectron spectroscopy (XPS), which was carried out in an ion-pumped chamber (evacuated to $2.66 \times 10^{-7}$ Pa) of an Escalab5 (UK) spectrometer, employing MgK$\alpha$ radiation (binding energy (BE) = 1253.6 eV). Fig. 3a and Fig. 3b display the XPS results for as-prepared Co$_2$P. The binding energy (BE) of Co$_{2p}$ is about 778.6 eV, close to the BE of elemental Co, which is nearly 778.3 eV. This indicates that the active valence of Co is comparatively low and almost close to zero, which is consistent with the structure of $\beta$-Co$_2$P. Moreover, the BE peaks of 2s, 3s and 3p are all observed in Fig. 3a and accordant with the typical values. The BE value of P$_{2p}$ is only 130.0 eV, close to the BE value of elemental phosphorus (129.1 eV). From the integral peak areas of Co and P in the spectra of XPS, the product seems to be rather pure with the molar ratio of Co:P = 1.993:1, which is close to the chemical formula of Co$_2$P.

Fig. 2. TEM images of $\beta$-Co$_2$P nanorods obtained at different conditions: (a) $T_r = 180$ °C, 48 h; (b) $T_r = 220$ °C, 72 h.

The magnetic susceptibility measurement was performed in the temperature range of 5 to 300 K under 500 Oe on a commercial superconducting quantum interference device (SQUID). Plots of $\chi_m$ and $\chi_m T$ vs. $T$ are shown in Fig. 4. For the sample of $\beta$-Co$_2$P, the room temperature $\chi_m T$ value is significantly lower than that expected for uncoupling cobalt ions. Moreover, $\chi_m T$ decreases with decreasing temperature and almost vanishes when temperature approaches zero. This means that between the adjacent cobalt ions through P ions there is a strongly coupled antiferromagnetic interaction. For a single crystal of $\beta$-Co$_2$P, though, the atomic magnetic moments of tetrahedral Co (3f) and pyramidal Co (3g) sites are quite different,
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the neighboring cobalt ions are unparallel and antiferromagnetic on the whole (001) face, resulting in a net moment of 0 $\mu_B$ in this hexagonal structure [20]. On the other hand, as shown in Fig. 4, $\beta$-Co$_2$P displays paramagnetic properties because the Co ions are completely pyramidal [21]. Moreover, from the field dependence of the magnetization of $\beta$-Co$_2$P nanorods at 5 K, shown in the inset of Fig. 4, the rather unusual shape of this M-H curve possibly indicates that this material is comprised of a combination of weak magnetic and antiferromagnetic constituents, called canted antiferromagnetic state. When the particle size of $\beta$-Co$_2$P reduces to hundreds of nanometers, the magnetic coupling interaction at the interface between both of those nanorods is enhanced.

Furthermore, imperfect crystallization of $\beta$-Co$_2$P observed from Fig. 2 also leads to the improved magnetic coupling. These two reasons may lead to the weakly ferromagnetic interaction in low field of the $\beta$-Co$_2$P nanorods and, hence, the canted antiferromagnetic state.

Fig. 4. ZFC magnetization as a function of temperature in 500 Oe. The inset shows the magnetization of $\beta$-Co$_2$P as a function of field.

4. Conclusion

In summary, a novel solvothermal method was introduced for the preparation of nanorod-like $\beta$-Co$_2$P. This kind of $\beta$-Co$_2$P has a stable high-temperature phase and displays the canted antiferromagnetic state due to the reduction of dimensions and imperfect crystallization.

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