A Safe Low Temperature Route to Nanocrystalline Transition Metal Arsenides

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(Received October 25, 1999; CL-990912)

Nanocrystalline FeAs, CoAs and NiAs were prepared by keeping the mixture of $FeCl_3$, $CoCl_2$ or $NiCl_2$ with arsenic and KBH_4 in ethylenediamine (en) at 100 °C for 4 h, respectively. X-Ray powder diffraction (XRD) patterns and transmission electron microscope (TEM) images show that the products are orthorhombic FeAs, CoAs and hexagonal NiAs, respectively, and all are well crystalline in nanometers.

Compound semiconductors, mainly metal pnictides, have a wide variety of applications such as compact displayers,[1] satellite TV receivers[2] and optical fiber.[3] Compared with III-V semiconductors, transition metal pnictides have many special electrical, mechanical and anticorrodating properties.[4] Among them, iron arsenides have attracted scientists' attention for a long time because of its technological importance as semiconductors,[5] secondary high-temperature batteries[6] and catalysts.[7]

The most straightforward way to synthesize the transition metal arsenides, as we know, is the direct combination of elemental metal and arsenic at high temperature.[4] Recently, Parkin and co-workers synthesized a series of metal arsenides by solid state metathesis (SSM) reactions with alkaline metal pnictides and metal halides as precursors at a typical temperature of 500 °C. However, only a mixture of FeAs and Fe_2As was reported to be obtained by this method.[8]

In order to decrease the temperature and alleviate the time and energy cost, some new approaches have been introduced to prepare inorganic materials. For example, using a solution-liquid-solid (SLS) mechanism, Trentler et al. obtained InP and InAs at 111-201 °C and 203 °C respectively.[9] However, the very toxic gases, PH_3 and AsH_3 had to be used, in the process. Solvothermal co-reductions (STCR) method was used to prepare nanocrystalline FeAs[10] at 150-180 °C, while another toxic reagent, $AsCl_3$ had to be used. The use of AsH_3 and $AsCl_3$ is of particular concern due to their carcinogenic and mutagenic properties. Considering the order of toxicity given by Penrose,[11] R_3As(R = H, Me, Cl, etc.) > As_2O_3 (As(III)) > $(RAsO)_n$ > As_2O_5 (As(V)) > $R_nAsO(OH)_{3-n}$ (n =1, 2) > R_4As^+ > As (0), we give a safe route in eq 1. to prepare the transition metal arsenides such as FeAs, CoAs and NiAs at 100 °C. This route has a further advantage that the reactants are readily available.

$$MCl_x + As + KBH_4 \xrightarrow{en} MAs + KCl + BH_3 + H_2 \quad (1)$$
$$M = Fe\ (x = 3), \quad M = Co\ or\ Ni\ (x = 2)$$

Reduction of metal salts with hydroorganborates is very useful to prepare finely divided powders of metals and alloys.[12] Here we report potassium borohydride reducing route to prepare MAs (M = Fe, Co and Ni) nanocrystalline.

In this approach, all reagents were of analytical grade, and the metal chlorides were purified by refluxing in thionyl chloride ($SOCl_2$) for 45 min before used. FeAs was prepared as follows : 40 ml of ethylenediamine, 0.8125 g (5 mmol) of $FeCl_3$ and 0.375 g (5 mmol) of arsenic were added to a 50 ml flask, and then the mixture was ultrasonically mixed for 4 h before putting 0.807 g (15 mmol) of KBH_4 into the flask .The mixture was transferred to a Teflon-lined autoclave at once. It was maintained at 100 °C for 24 h, and then cooled to room temperature naturally. The CoAs and NiAs were prepared analogously to FeAs by using $CoCl_2$ and $NiCl_2$ with the molar ratio MCl_2 : As : KBH_4 = 1 :1 : 2, (M = Co, Ni, respectively). The products were filtered out, washed with distilled water and absolute alcohol in sequence, and then dried in vacuum at room temperature for 4h.

All the products have been characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM) examinations.[13] XRD patterns for FeAs, CoAs and NiAs are shown in Figure 1, which are in agreement with literature.[14] Average crystalline sizes as determined by Scherrer equation based on the XRD linewidths are recorded in Table 1. TEM images show nearly monodisperse plate morphology of the

Table 1. Characterization of products

Product	Phase	Lattice parameters / Å		TEM Size / nm
		Experiment	Literature	
FeAs	Ortho- rhombic	a=5.451 b=6.011 c=3.151	a=5.436 b=6.024 c=3.372	35
CoAs	Ortho- rhombic	a=3.484 b=3.895 c=5.262	a=3.458 b=5.869 c=5.292	30
NiAs	Hexag- onal	a=3.618 c=5.018	a=3.622 c=5.013	20

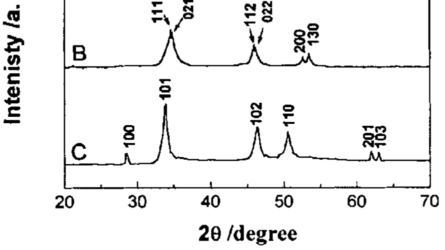

Figure 1. XRD patterns of as-prepared products: (A) FeAs, (B) CoAs, (C) NiAs.

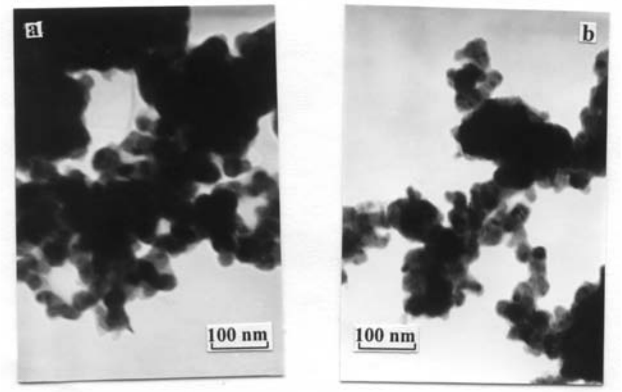

Figure 2. TEM images of as-prepared products: (a) FeAs, (b) NiAs.

products. As examples, TEM images for FeAs and NiAs are shown in Figure 2. Particle sizes determined by TEM are also recorded in Table 1, which are in accordance with average size estimated from XRD patterns.

In order to investigate the influence of different solvents, we substituted ethylenediamine for benzene, heptane and CCl_4, respectively, under similar condition. We found that in benzene, heptane and CCl_4, no arsenides can be obtained. Considering the difference in the coordinating ability of ethylenediamine and benzene, heptane or CCl_4, we proposed a possible formation mechanism as follows (taking the FeAs as an example) :

$$FeCl_3 + x(en) \rightarrow [Fe(en)_x]^{3+} + 3Cl^- \qquad (2)$$

$$2[Fe(en)_x]^{3+} + 6KBH_4 \rightarrow 2Fe + 6BH_3 + 3H_2 + 6K^+ + 2x(en) \qquad (3)$$

$$Fe + As \rightarrow FeAs \qquad (4)$$

The reaction mechanism can be rationalized and the intermediate product is confirmed as elemental iron by the following experiments: If the $FeCl_3$, As, KBH_4 and ethylenediamine were added together into a flask, mixed by ultrasonic treatment at room temperature, and then maintained at 100 °C for 24 h, the product was not the metal arsenides, but the mixture of metallic iron and arsenic powder, as confirmed by XRD results. Since, at the room temperature, newly formed iron atoms reduced with KBH_4 cannot react with arsenic. However, when the temperature is not lower than 100°C, the newly formed iron atoms reduced with KBH_4 are active enough to combine with arsenic immediately to form corresponding metal arsenides.

Financial support from the Chinese National Foundation of Natural Science Research and Huo Yingdong Foundation for Young Teachers is gratefully acknowledged.

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14 Joint Committee on Powder Diffraction Standards (JCPDS), File No.12-799 FeAs; 9-94 CoAs; 31-900 NiAs.