

A Safe Low Temperature Route to Nanocrystalline Transition Metal Arsenides

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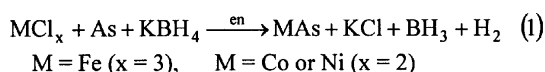
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Nanocrystalline FeAs, CoAs and NiAs were prepared by keeping the mixture of FeCl₃, CoCl₂ or NiCl₂ with arsenic and KBH₄ in ethylenediamine (en) at 100 °C for 4 h, respectively. X-Ray powder diffraction (XRD) patterns and transmission electron microscope (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 displays,¹ satellite TV receivers² and optical fiber.³ Compared with III-V semiconductors, transition metal pnictides have many special electrical, mechanical and anticorrosion 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 batteries⁶ 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 Fe₂As 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, PH₃ and AsH₃ had to be used, in the process. Solvothermal co-reductions (STCR) method was used to prepare nanocrystalline FeAs¹⁰ at 150–180 °C, while another toxic reagent, AsCl₃ had to be used. The use of AsH₃ and AsCl₃ is of particular concern due to their carcinogenic and mutagenic properties. Considering the order of toxicity given by Penrose,¹¹ R₃As(R = H, Me, Cl, etc.) > As₂O₃ (As(III)) > (RAsO)_n > As₂O₅ (As(V)) > R_nAsO(OH)_{3-n} (n = 1, 2) > R₄As⁺ > 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.



Reduction of metal salts with hydroorganoborates 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 (SOCl₂) for 45 min before used. FeAs was prepared as follows : 40 ml of ethylenediamine, 0.8125 g (5 mmol) of FeCl₃ 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 KBH₄ 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 CoCl₂ and NiCl₂ with the molar ratio MCl₂ : As : KBH₄ = 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	Orthorhombic	a=5.451	a=5.436	35
		b=6.011	b=6.024	
		c=3.151	c=3.372	
CoAs	Orthorhombic	a=3.484	a=3.458	30
		b=3.895	b=5.869	
		c=5.262	c=5.292	
NiAs	Hexagonal	a=3.618	a=3.622	20
		c=5.018	c=5.013	

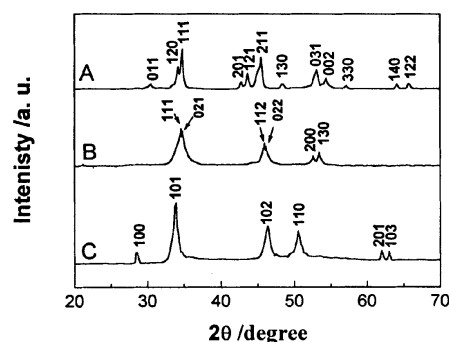


Figure 1. XRD patterns of as-prepared products: (A) FeAs, (B) CoAs, (C) NiAs.

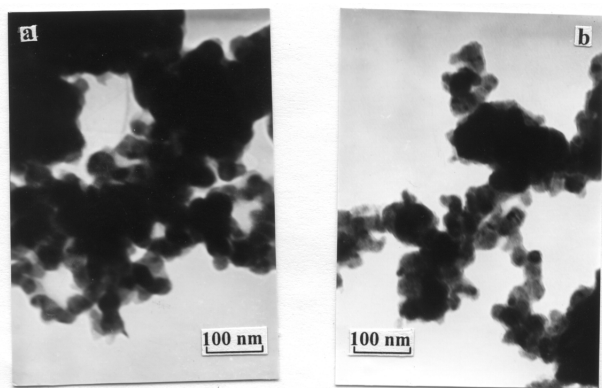
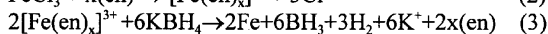
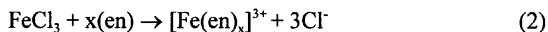


Figure 2. TEM images of as-prepared products: (a) FeAs, (b) NiAs.

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) :



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.

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- 13 XRD patterns were obtained on a Japan Rigaku D/Max γA rotation anode X-ray diffractometer with Ni-filtered $\text{CuK}\alpha$ radiation ($\lambda=1.54178 \text{ \AA}$). TEM measurements were made on a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 KV.
- 14 Joint Committee on Powder Diffraction Standards (JCPDS), File No.12-799 FeAs; 9-94 CoAs; 31-900 NiAs.