The Solvothermal Synthesis for Nanocrystalline $FeIn_2S_4$ at Low Temperature

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5 nm thiospinel $FeIn_2S_4$ nanocrystallines were prepared through a solvothermal process at 280 ℃. Powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) reveal that the product was nanocrystalline $FeIn_2S_4$, with cubic cell, and uniform spherical particle morphology. The factors to the formation of uniform $FeIn_2S_4$ nanocrystallines with a narrow size distribution were discussed also.

Nanometre-scale structures and molecular materials have attracted interest as potential building blocks for future generation electronic devices of greatly reduced size.[1] Such materials are characterized by their physical and chemical properties which particularly depend on their grain size and shape.[2] Thus the low temperature synthesis of uniform nanocrystallines is of interest to many material scientists.[3] In this paper, we describe a novel solvothermal process for synthesizing $FeIn_2S_4$ nanocrystalines at 280 ℃.

Semiconductor $FeIn_2S_4$ is a representative compound of a series of indium thiospinels that were first prepared by Hahn in 1950 using a direct combination of binary sulfides.[4] More recently, many scientists have studied the magnetic, optical, dielectric properties of $FeIn_2S_4$.[5-7] Fabrication of the type $II-III_2-VI_4$ was conventionally through direct element reaction at 800 ℃-1000 ℃.[4,5,8] To our knowledge, no reports have been published about the preparation of $FeIn_2S_4$ at synthetic conditions of lower temperature and no $FeIn_2S_4$ nanocrystallines are reported to have been formed. Here we propose a new one-step method for synthesizing $FeIn_2S_4$ nanocrystallines in solution at low temperature, by using benzene as the solvent. As known, preparation methodology has an important effect on material microstructure and physical properties.[9,10] There are various kinds of preparation processes, but the solution chemical synthesis technique is particularly effective because phase homogeneity, particle size and distribution, and morphology can be well controlled.[9,10] We have designed a simple method for the preparation of $FeIn_2S_4$ nanocrystallines, with a narrow size distribution, under solvothermal conditions. The synthetic reaction was carried out in an autoclave, associated with the reaction:

$$FeCl_3 + 3In + 4S \longrightarrow FeIn_2S_4 + InCl_3$$

This process did not require absolutely nonaqueous condition, and using $FeCl_3$ (the unhydrated form) or $FeCl_3 \cdot 6H_2O$ as the reactant both resulted in the formation of $FeIn_2S_4$ nanocrystallines.

In a typical experiment, $FeCl_3 \cdot 6H_2O$, In, and S with theoretical molar ratios were put in a titanium alloy autoclave of 50 ml capacity that was filled with benzene to 80% of the total volume. The autoclave was maintained at 280 ℃ for 12 h and then cooled to room temperature. After filtering and washing with absolute alcohol, a dark gray product was collected.

$FeIn_2S_4$ is an inverse cubic spinel, in which Fe^{2+} ions only occur in the B sites (octahedral site) and In^{3+} ions are equally distributed among the A sites (tetrahedral site) and B sites.[5]

X-Ray powder diffraction (XRD) was carried out using a Rigaku DmaxϒA X-ray diffractometer with Cu Kα radiation (λ=1.54178 Å). Figure 1 shows the XRD pattern of the product prepared in benzene. All peaks can be indexed to the cubic cell of $FeIn_2S_4$ with lattice constant a = 10.63 Å which is near to the reported value (a=10.62 Å, JCPDS card, No.16-170). No impurities were detected. The broadening of these diffraction peaks suggests that the obtained sample be of nanometer scale. The average particle size of the product was calculated to be 5 nm by the Scherrer formula.

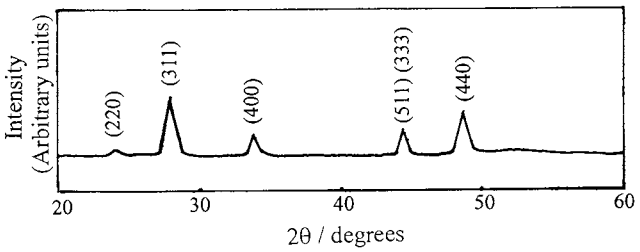

Figure 1. X-ray diffraction pattern of the sample prepared in benzene.

The morphology of the final product was observed by transmission electron microscopy (TEM) using on Hitachi H-800 transmission electron microscope. The TEM image of the $FeIn_2S_4$ powder, prepared at 280 ℃ using benzene as the

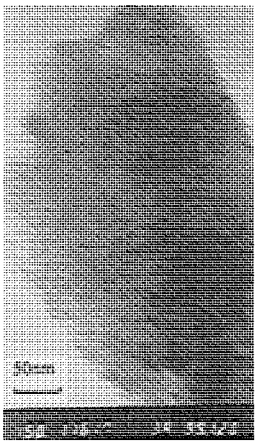

Figure 2. Transmission electron microscopy image of the sample prepared in benzene.

solvent, is shown in Figure 2. The image reveals that the sample consists of uniform spherical grains with particle size ranging from 3 nm to 6 nm, which is in agreement with the result obtained by XRD.

In our process, when only $FeCl_3$ and S were used as the reactants, the product was determined to be iron sulfide. This experimental result indicates that the formation of iron sulfide could be attributed to the dismutation of S. To understand the possible mechanism of the synthetic reaction, we changed the reactants but with no change of the solvent, reaction temperature and time. When Fe and S were used as the reactants, the product was still iron sulfide. However, the reaction between Fe, In, and S at the same experimental conditions did not produce $FeIn_2S_4$. So the formation of $FeIn_2S_4$ was not through the reaction between iron sulfide, In, and S. The use of $FeCl_3$ was very important to the synthesis of $FeIn_2S_4$. The by-product of the reaction between $FeCl_3$ and S was sulfur chloride that could make indium activate,[11] which might be the critical factor to the formation of $FeIn_2S_4$.

The product of the one-step reaction for $FeIn_2S_4$ nanocrystallines comprises uniform-sized grains, which reflects the homogeneous pressure under solvothermal conditions. In this process, with an increase of reaction temperature, the liquidation of metal In and dissolution of S in benzene will result in the synthetic reaction becoming a solid-liquid-solution (SLS) reaction,[12] which has some effect on the formation of uniform $FeIn_2S_4$ nanocrystallines due to the large surface in contact between liquid state reactants and solid state reactant.

Many experimental conditions, such as reaction temperature and time, and solvent, play a significant role in this solvothermal synthesis. In the formation of $FeIn_2S_4$ nanocrystallines, reaction temperature and time are very important. A temperature above 250 ℃ is essential to produce well crystallized $FeIn_2S_4$, although a temperature of 200℃ also can result in the formation of $FeIn_2S_4$ with poor crystallinity. A temperature higher than 350 ℃ is not needed and will lead to the growth of grains. In our process, a temperature of 280 ℃ was chosen. To make the synthetic reaction proceed completely, the reaction time should be no shorter than 5 h, although further prolongation of the reaction time is not important to the formation of $FeIn_2S_4$ nanocrystallines. In this solvothermal process, the function of different solvents in the synthetic process was also studied. Three different organic compounds (benzene, pyridine, and ethylenediamine) were used as solvents, with no change of other experimental conditions, and each the resultant product was determined to be $FeIn_2S_4$ nanocrystallines. However, in the cases of ethylenediamine and pyridine, the products had a preferred orientation and the morphologies were irregular. This may be attributed to the coordination of the solvent that is prone to result in a rod shape for the final product.[13,14]

In summary, 5 nm $FeIn_2S_4$ nanocrystallines, with a narrow size distribution, were successfully prepared through a benzene-thermal process. The synthetic temperature 280 ℃ is, to our knowledge, the lowest used to obtain nanocrystalline $FeIn_2S_4$. This method may also be applied to the preparation of other ternary sulfides and selenides; not only thiospinels, but also chalcopyrites.

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