Solvothermal Synthesis of $NiS_{2-x}Se_x$ Nanocrystallines

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$NiS_{2-x}Se_x$ nanocrystallines ($0 \le x \le 2$) was successfully synthesized by solvothermal method at 180–200 °C. It was found that both temperature and solvent have important effects on the formation of $NiS_{2-x}Se_x$ nanocrystallines.

Metal-insulator transitions (MIT) caused by strong electron correlation have been the subject of extensive research continuous in recent decades,[1] but the discovery of superconductivity and related MIT in some copper oxide based materials has led to increase attention to this phenomenon. The $NiS_{2-x}Se_x$ system is believed to be a good candidate to obtain valuable information about MIT and to shed light on the physics of the new superconductors.[2] The $NiS_{2-x}Se_x$ system has been extensively investigated due to its rich phase diagram and interesting transport properties.[3–6] For $x < 0.4$ it is a semiconductor at all temperatures. For $x > 0.6$ it is metallic at all temperature. For $0.4 < x < 0.6$ it is a semiconductor at high temperature, but under a critical temperature that depends on x, the materials undergo an insulator-metal transition. At the transition there is no any apparent structural distortion.[7–9]

$NiS_{2-x}Se_x$ crystals are usually prepared by the chemical vapor transport operation with involving chlorine or bromine as the transport agent[4,5] or the Te flux method[9] at 730–780 °C.

Semiconductor nanoparticles have some special characteristics due to their large surface-to-volume ratio, quantum size effect, and dielectric confinement effect.[10–15] They are expected to exhibit a variety of new spectroscopic features, including sharper absorption spectra, enhanced exciton and impurity binding energies, and modified electron–phonon coupling, which depend sensitively on both size and shape,[16,17] are of both fundamental and technological interest.

During recent years, the solvothermal method was emerging as an effective synthetic technique for chalcogenides.[18] In this paper, we report the synthesis of $NiS_{2-x}Se_x$ nanocrystallines at much lower temperature via a solvothermal method.

Analytically pure $NiCl_2 \cdot 6H_2O$, elemental S and Se powder (molar ratio 1: 2–x: x, $0 \le x \le 2$) were put into a 50 mL autoclave, which filled with solvent up to 80% of total volume. In the experiments ethylenediamine (en) and pyridine (py) (volume ratio 1:1) were selected as the reaction media. The autoclave was maintained at 180–200 °C for 8–10 h and cooled naturally to room temperature. The products were filtered, washed with anhydrous alcohol and distilled water, and dried in a vacuum at 60 °C for 2 h.

X-ray powder diffraction (XRD) pattern was obtained on a Rigaku Damax γA X-ray diffractometer with Cu Kα radiation (λ=1.54178 Å). Transmission electron microscopy (TEM) images were taken with a Hitachi H-800 transmission electron microscopy, using an accelerating voltage of 200 kV.

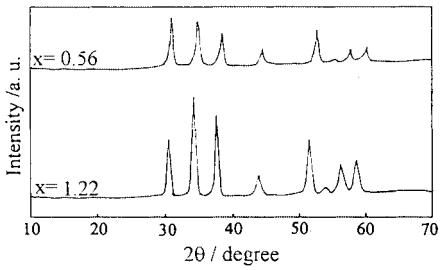

Figure 1. XRD patterns of the as-prepared $NiS_{2-x}Se_x$.

Figure 1 shows the XRD pattern of as-prepared $NiS_{2-x}Se_x$ (x=0.56, 1.22). Se content x is determined from the energy dispersion X-ray fluorescence analysis of the as-prepared samples. The $NiS_{2-x}Se_x$ system characterized as pyrite type structure. Figure 2 is the energy dispersion X-ray fluorescence analysis (EDAX) spectrum of the as-prepared $NiS_{2-x}Se_x$ (x=0.56, 1.22).

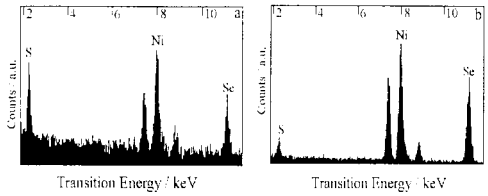

Figure 2. EDAX spectrum of as-prepared $NiS_{2-x}Se_x$. (a) x=0.56; (b) x=1.22.

The TEM images of $NiS_{2-x}Se_x$ (x = 0.56, 1.22) are shown in Figure 3. It can be seen that $NiS_{2-x}Se_x$ consisted of particles with an average size of 10 nm. The particles are easily coalesced. The size of $NiS_{2-x}Se_x$ ($x > 1.6$) increased as the Se content increase.

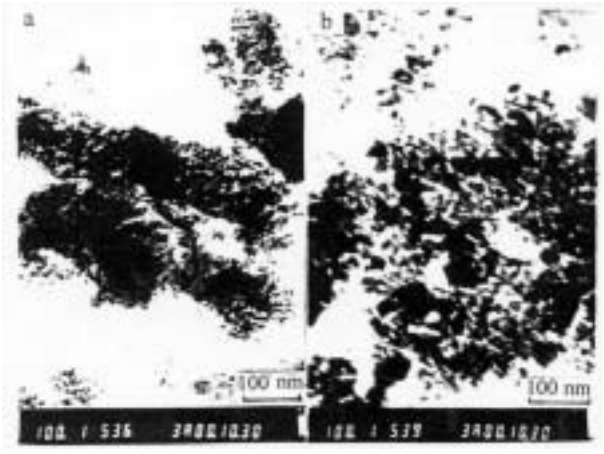

Figure 3. TEM images of as-prepared $NiS_{2-x}Se_x$. (a) x=0.56; (b) x=1.22.

It was found that both of temperature and solvent play an important role on the formation of $NiS_{2-x}Se_x$ ($0 \le x \le 2$) nanocrystallines. In our present study, no NiS_2 or $NiSe_2$ can be obtained if the reaction temperature is lower than 140°C. Therefore, we believe that more energy will be needed solid solution of $NiS_{2-x}Se_x$ in comparison with that of NiS_2 or $NiSe_2$ single phase. Our result showed that the miscellaneous diffraction peaks would be present in the X-ray diffraction patterns if the reaction temperature lower than 180 °C, indicating that the solid solution process does not take place effectively. If the higher temperatures ($T > 180$ °C) are employed and py and en are selected as solvent, the composition range for the solid solution of $NiS_{2-x}Se_x$ is much extended. If a single solvent is used, the composition range is very limited. For example, no $NiS_{2-x}Se_x$ ($x > 0.6$) can be obtained when py is selected as a solvent; No $NiS_{2-x}Se_x$ ($x < 1.6$) can be obtained when en is selected as a solvent. A possible reason is that the product of the reaction between $NiCl_2 \cdot 6H_2O$ and S in en at 180–200 °C is NiS and NiS_2. No $NiSe_2$ can be obtained in py at 180–190 °C. The effect of other solvents such as toluene, tetrahydrofuran, benzene on the formation of $NiS_{2-x}Se_x$ nanocrystallines was also studied. However, the reaction among $NiCl_2 \cdot 6H_2O$, S and Se did not occur when those solvents selected as reaction media. The optimum condition is py and en (volume ratio 1:1) selected as solvent at 190–200 °C.

In a summary, $NiS_{2-x}Se_x$ ($0 \le x \le 2$) nanocrystallines were successfully prepared through a solvothermal route at relatively low temperature. It was found that both reaction temperature and solvents play a key role in the formation of $NiS_{2-x}Se_x$ nanocrystallines. The MIT properties of as-synthesized $NiS_{2-x}Se_x$ nanocrystallines are in progress.

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