Selective Synthesis and Magnetic Properties of α-MnSe and MnSe₂ Uniform Microcrystals

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A facile and selective route based on a precipitate slow-release controlled process was developed to produce both high-quality $MnSe_2$ and α -MnSe uniform microcrystals in aqueous solution at low temperatures (100– 180 °C). The magnetic properties of the two samples were investigated in detail. This synthetic method will have potential applications in material science, especially in fabricating diluted magnetic semiconductors. These uniform microcrystals might be useful in microdevices, seed crystals, and magnetic cells.

Introduction

Transition metal chalcogenides and dichalcogenides have drawn considerable attention because of their important optical, electrical, and transport properties.^{1,2} Their conductive behavior ranges from semiconductor to metallic, and they evidence a wide range of magnetic properties.^{3,4} MnSe and MnSe₂ have attracted great interest especially because of their critical magnetic functions, for example, in the application of fabricating diluted magnetic semiconductors (DMSs).^{5–7} With the introducing of Mn²⁺, the host semiconductor will exhibit unique optical and magnetic properties based on the exchange interaction of sp–d band electrons.

Molecular beam epitaxy (MBE)⁸ or organometallic vaporphase epitaxy (OMVPE)⁹ method is often employed in the traditional routine to synthesize α -MnSe and MnSe₂, including the introduction of Mn²⁺ into DMSs. Decker et al.¹⁰ have synthesized α -MnSe by using high-purity Mn metal reacting with elemental Se at 900 °C in a quartz tube for 20 h with the existence of catalyst (I₂). MnSe₂ can also be obtained by using stoichiometric Mn and Se at 550 °C through this method.¹¹ (NH₄)₂Se or H₂Se is often used to provide Se source in the solution-phase synthesis of MnSe.¹¹ These methods usually need complex apparatus, severe reaction conditions, and toxic and sensitive raw materials, which may restrict the wide development of researches and applications.

In this paper, we designed a precipitate slow-release controlled synthetic method in aqueous solution, which can conveniently produce both high-quality MnSe₂ and α -MnSe uniform microcrystals at low temperatures (100–180 °C). Na₂SeO₃, MnSO₄, and the reductant N₂H₄•H₂O are used as reactants in this hydrothermal method. The high yields, simple reaction apparatus, and low reaction temperature give this novel method a good prospect in future applications.

Experimental Section

All chemicals in this work, such as manganese sulfate (MnSO₄), sodium selenite (Na₂SeO₃), and hydrazine hydrate

(N₂H₄·H₂O, 80%) were A. R. regents from the Beijing Chemical Factory, China. They were used without any pretreatment.

To prepare α -MnSe and MnSe₂ microcrystals, MnSO₄ (1.51 g, 0.01 mol) was put into a Teflon-lined autoclave of 100 mL capacity and dissolved in 60 mL of deionized water. A total of 0.86 g (0.005 mol) of Na₂SeO₃ and 10 mL of hydrazine hydrate (N₂H₄·H₂O) were added into the autoclave. After stirring for 5 min, the autoclave was sealed and heated at 100 °C (for MnSe₂) or 180 °C (for α -MnSe) for about 24 h. The autoclave was allowed to cool to room temperature naturally after heat treatment. The system was transferred into 200 mL of citric acid (1 M) solution and stirred until Mn(OH)₂ precipitation dissolved. The sample (black color for MnSe₂ and dark brown color for α -MnSe) was collected by filtration, washed with deionized water and absolute ethanol, and then dried at 60 °C. The yields of both of the two products are about 90% based on the calculation of Na₂SeO₃.

The obtained samples were characterized on a Brucker D8advance X-ray powder diffractometer (XRD) with Cu K α radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) were taken on a JEOL JSM-6301F scanning electron microscope operated at 20 kV. DC magnetic susceptibility measurements were made on a Maglab 2000 superconducting quantum interference device (SQUID) magnetometer.

Results and Discussion

MnSe crystallizes in three forms (α -, β -, and γ -MnSe). The α -MnSe, which has the NaCl structure (Figure 1a), is the thermodynamically stable phase.¹¹ MnSe₂ has a cubic pyrite structure (Figure 1b), which has a close resemblance with NaCl structure and contains discrete Se₂ groups. The Mn atoms are on octahedral sites with six nearest-neighbor Se atoms, whereas the Se coordination is tetrahedral (consisting of one selenium and three manganese atoms). If the Se₂ groups are changed by Se atoms in the middle of the edges, MnSe structure will be obtained.

Figure 2 shows the XRD patterns obtained from the two assynthesized samples of $MnSe_2$ and α -MnSe microcrystals, which indicate that they are both pure-phase compounds. The strong and narrow peaks show good crystallinity of them. The lattice parameters of $MnSe_2$ (Figure 2a) and α -MnSe (Figure 2b) were

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Figure 1. Crystal structures of (a) α -MnSe and (b) MnSe₂.



Figure 2. Powder X-ray diffraction patterns of (a) $MnSe_2$ and (b) α -MnSe.

calculated as a = 6.417 Å (JCPDS 73-1525) and a = 5.462 Å (JCPDS 11-0683), respectively.

SEM images of the two samples, which can show information on the quality of individual microcrystals, are given in Figure 3. The sample of MnSe₂ (Figure 3a-c) is comprised of many uniform cubic microcrystals with almost the same edge size. Although desquamation phenomenon can be noticed on the

surface of some microcrystals, these cubes have good crystallinity, which corresponds to the XRD results. The average edge size of these cubes is about 30 μ m (Figure 3c), for which was calculated the average volume of about 27000 μ m³. From the staircase surface of some cubes, it seems that MnSe₂ crystals may grow on the basis of layer structures. The sample of α -MnSe is an aggregation of uniform ball-like microcrystals (Figure 3d-f), with average radius of about 3 μ m. The uniformity and similar dimension of them show a good growth environment of α -MnSe crystals, which indicate the good crystallinity of these spheres from the other aspect. Figure 4 shows the energy dispersion spectroscopy (EDS) measurements on these two samples. The x-axis shows the energy of the X-quantum photons, which can be used to identify the elements. Different elements will have different energy of the X-quantum photons. The y-axis shows the quantities of the X-quantum photons, which can reflect the relative content of elements. The characteristic peaks for both Se and Mn are observed (Mn, about 6 keV; Se, about 11 and 1.5 keV). The atomic ratios are calculated to be 2:1 (MnSe₂) and 1:1 (α -MnSe) by the comparisons of relative areas under the peaks of Se and Mn.

Using soluble Na₂SeO₃ as the Se source to synthesize selenides is a novel and effective method. Na₂SeO₃ will dissociate itself and form SeO₃²⁻ in aqueous solution, which can be reduced to Se very quickly upon heating.¹² Compared to commercial Se powder, the newly produced Se (even Se_n molecules dissolved in solution before their aggregation) is much more reactive, and it is easier to produce Se²⁻ through disproportionation under alkaline conditions.¹³ In our experiments, the whole process (from SeO₃²⁻ to Se²⁻) is found to be completed in 2 h in the presence of N₂H₄ as reductant (pH \approx 11) at 100–180 °C.¹⁴ Nothing but unreacted Se and Mn(OH)₂ had been obtained in our experiments if commercial Se powder was used as raw material instead of Na₂SeO₃.

Before the heat treatment, Na₂SeO₃ will first react with Mn²⁺ and form MnSeO₃ ($K_{sp} = 5.4 \times 10^{-8}$) precipitate, which can dissociate in water and form SeO₃²⁻ slowly. The proposed steps to form MnSe₂ (at 100 °C) can be described as follows:

$$Na_2SeO_3 + Mn^{2+} \rightarrow 2Na^+ + MnSeO_3(\downarrow)$$
 (1)

$$MnSeO_3 \xrightarrow{slow release} Mn^{2+} + SeO_3^{2-}$$
 (2)

$$\text{SeO}_{3}^{2-} + \text{N}_{2}\text{H}_{4} \rightarrow \text{Se} + \text{N}_{2} + \text{H}_{2}\text{O} + 2\text{OH}^{-}$$
 (3)

$$3Se + 6OH^{-} \rightarrow 2Se^{2-} + SeO_3^{2-} + 3H_2O$$
 (4)

$$\operatorname{Se}^{2^{-}} + \operatorname{Se} + \operatorname{Mn}^{2^{+}} \to \operatorname{MnSe}_{2}(\downarrow)$$
 (5)

The slow-released SeO₃²⁻ will soon be reduced in step 3. The in-situ produced ultrafine Se particles with high reactivity form Se²⁻ much more easily through the disproportionating reaction (step 4). The Se²⁻ formed in step 4 will combine with one Se atom produced in step 3 to form Se₂²⁻ (Se + Se²⁻ \rightarrow Se₂²⁻). This is just like the formation of polysulfide ions in aqueous solution. The MnSe₂ product is finally obtained through the precipitation reaction of Se₂²⁻ + Mn²⁺ \rightarrow MnSe₂ (step 5). Because the K_{sp} of MnSe₂ is smaller than that of MnSeO₃, step 5 might be the driving force of the whole set of reactions. The SeO₃²⁻ generated in step 3 will be reduced by hydrazine again and is finally consumed completely to form the product because of the excess of Mn²⁺. In the experiments, long reaction time (24 h is selected) is needed to convert all MnSeO₃ to MnSe₂ and favor the growth of high-quality and large MnSe₂ micro-



Figure 3. SEM images of as-synthesized (a, b, c) $MnSe_2$ and (d, e, f) α -MnSe microcrystals with different magnifications.



Figure 4. EDS analysis of $MnSe_2$ and α -MnSe samples. Characteristic peaks for both Se and Mn are observed. The molar ratios of Se and Mn are shown in the inset. The peak of Au is observed because the samples are coated by Au film for good electrical conductivity.

crystals. On the basis of our experimental results, step 2 may play an important role in the formation of uniform $MnSe_2$ microcrystals. The slow dissociation of $MnSeO_3$ into Mn^{2+} and SeO_3^{2-} makes the formation of the initial $MnSe_2$ nuclei very slow, which forms a good basis for the crystallization of $MnSe_2$. Well-crystallized uniform microcrystals will be produced after a long period reaction.

In our experiments, MnSe₂ is only found for syntheses below about 120 °C. When the reaction temperature is raised to 140 °C, the product only contains α -MnSe. To get phase-pure α -MnSe and improve the crystallinity of the product, 180 °C is chosen for the synthesis of α -MnSe. To understand the reaction process more clearly, additional experiments have been performed. The autoclave was first put into a baking oven at 100 °C, just the same condition as MnSe₂. After 24 h, temperature



Figure 5. The evolution of the XRD patterns of the products with different reaction times at 180 °C: (*) MnSe₂; (#) α -MnSe.

was increased to 180 °C and maintained for another 24 h. α -MnSe was found to be the final product. When MnSe₂ was isolated after the first reaction step at 100 °C, put into an autoclave only containing deionized water, and heated at 180 °C for 24 h, no reaction happened. This indicates that the reductant N₂H₄ and the excess Mn²⁺ in the system play an important role in the formation of α -MnSe at higher temperatures. The α -MnSe product may result from the transition of MnSe₂.

To verify the formation mechanism of α -MnSe, the product was taken out after reaction for 3, 6, and 12 h at 180 °C and characterized by XRD (after dissolving the impurities of Mn(OH)₂ and MnSeO₃ by using excess ammonium citrate solution (5 M)). Figure 5 shows the XRD patterns of the products obtained at different stages. Only MnSe₂ peaks are found in the XRD pattern of the product after 3 h reaction. With the elongation of reaction time, the peaks of α -MnSe become stronger, along with the weakening of MnSe₂ peaks, which indicates the transition from MnSe₂ to α -MnSe. α -MnSe has become the main phase of the product after 12 h reaction. After 24 h, all MnSe₂ has been consumed and a pure phase of α -MnSe



Figure 6. Magnetic susceptibility, χ_m , and $\chi_m T$ vs temperature *T* plots for α -MnSe and MnSe₂: (a) $H = 10\ 000\ G$; (b) $H = 5000\ G$; (c) isothermal field dependence of the magnetization.

is produced (not shown in Figure 5). This transition can be explained from the crystal structures of them. From both energy and space-filling points of view, α -MnSe with the NaCl structure (Se/Mn = 1:1) is more stable than MnSe₂ with the pyrite structure (Se/Mn = 2:1). The Se₂ groups in the MnSe₂ structure are more reactive and the Se-Se bonds may be broken under appropriate conditions (N₂H₄ and excess of Mn²⁺). The released Se atoms will be converted to selenide in our reaction system. On the basis of the experiments above, long reaction time is also needed to convert MnSe₂ to α -MnSe completely, and the slow transition rate results in the good crystallinity of α -MnSe. On the other hand, the rate of the disproportionating reaction of Se (step 4) will be faster at 180 °C, which favors the formation of Se^{2–}. It is also possible that some of the α -MnSe is formed directly through the reaction of $Mn^{2+} + Se^{2-} \rightarrow MnSe$ after step 4.

The magnetic susceptibility measurements were performed in the temperature range 1.8-300 K under 5000 and 10 000 G, respectively. Plots of χ_m and $\chi_m T$ vs T are shown in Figure 6. The room-temperature $\chi_m T$ values (2.5 emu K mol⁻¹ for α -MnSe, 1.9 emu K mol⁻¹ for MnSe₂) are significantly lower than what was expected for a noncoupling high-spin Mn²⁺ ion (4.375 emu K mol⁻¹ with g = 2.0). In both cases, $\chi_m T$ decreases with the decrease of the temperature and vanishes when Tapproaches zero. The magnetic susceptibility obeys the Curie-Weiss law in the temperature range 120-300 K for α -MnSe and 50–300 K for MnSe₂ giving the Weiss constants of -216.8K for the former and -549.7 K for the latter. These features are characteristic of a considerably strong antiferromagnetic interaction between adjacent Mn²⁺ ions through Se²⁻ bridges. The $\chi_m - T$ curves ($H = 10\ 000\ G$) show a shallow maximum at 120 K for α -MnSe and an apparent maximum at 45 K for MnSe₂, and much more marked maxima are observed in the $\chi_{\rm m}-T$ curves measured in 5000 G (Figure 5b). The presence of the maxima indicates the occurrence of long-range antiferromagnetic order.15

Below $T_{\rm N}$, both compounds exhibit complicated magnetism. The susceptibilities in 5000 G undergo an abrupt upturn and display another maximum at liquid helium temperatures, whereas the 10 000 G data do not show such maxima. This magnetic behavior may suggest the occurrence of spin flop in the antiferromagnetic state, which would account for the abrupt increase in χ_m . This supposition could be confirmed by the measurements of isothermal field dependence of the magnetization as shown in Figure 6c. The magnetization at 1.8 K increases linearly with the field reaching 0.23 N β for α -MnSe and 0.12 N β for MnSe₂ at the highest accessible field of 7 T. These values are much lower than the saturation value of 4 N β for high-spin octahedral Mn²⁺ compounds, indicating an antiferromagnetic behavior for both compounds. The magnetization value at 7 T for MnSe₂ is lower than that for α -MnSe, which may be due to the stronger antiferromagnetic interaction in MnSe₂ as implied by the Weiss constants.

Conclusion

In summary, we have demonstrated a precipitate slow-release controlled synthesis method, which could produce high-quality α -MnSe and MnSe₂ microcrystals conveniently on a large scale. These microcrystals might have potential applications in microdevices, seed crystals, and magnetic cells among others. This synthetic method surely could be applied in fabricating diluted magnetic semiconductors (DMSs) and be carried out to synthesize other high-quality selenides, especially those that are difficult to obtain through conventional methods.

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References and Notes

(1) Ennaoui, A.; Fiechter, S.; Jaegermann, W.; Tributsch, H. J. Electrochem. Soc. 1986, 133, 97.

(2) Heulings, H. R., IV; Huang, X.; Li, J.; Yuen, T.; Lin, C. L. Nano Lett. 2001, 1, 521.

- (3) Jarrett, H. S.; Cloud, W. H.; Bouchard, S. R. B.; Fredericks, C. G.; Gillson, J. L. *Phys. Rev. Lett.* **1968**, *21*, 617.
 - (4) Mikkelson, J. C.; Word, A. J. Solid State Chem. 1971, 3, 39.
- (5) Norris, D. J.; Yao, N.; Charnock, F. T.; Kennedy, T. A. *Nano Lett.* **2001**, *1*, 3.
- (6) Levy, L.; Feltin, N.; Ingert, D.; Pileni, M. P. J. Phys. Chem. B 1997, 101, 9153.

(7) Suyver, J. F.; Wuister, S. F.; Kelly, J. J.; Meijerink, A. Nano Lett. **2001**, *1*, 429.

(8) Heimbrodt, W.; Goede, O.; Tschentsher, I.; Weinhold, V. Physica B 1993, 185, 357.

- (9) Tomasini, P.; Haidoux, A.; Tedenac, J. C.; Maurin, M. J. J. Cryst. Growth 1998, 193, 572.
- (10) Decker, D. L.; Wild, R. L. *Phys. Rev. B* 1971, 4, 10.
 (11) Xie, G. Y.; Yu, L. M.; Liu, B. Y. *Series of Inorganic Chemistry*; Chemical Engineering Publisher: China, 1998; Vol. 9, p 72.
- (12) Gates, B.; Yin, Y. D.; Xia, Y. N. J. Am. Chem. Soc. 2000, 122, 12582.

(13) Wang, C.; Zhang, W. X.; Qian, X. F.; Zhang, X. M.; Xie, Y.; Qian, Y. T. Mater. Chem. Phys. 1999, 2409, 1-4.

(14) This is resulted from our other work (submitted) that all sodium selenite has been converted into selenides (e.g., CdSe, CoSe, NiSe) within 2 h if we use an appropriate complexing agent to prevent SeO_3^{2-} from forming an insoluble selenite precipitate (CdSeO₃, CoSeO₃, NiSeO₃) before reacting.

(15) Escuer, A.; Cano, J.; Goher, M. A. S.; Journaux, Y.; Lloret, F.; Mautner, F. A.; Vicente, R. Inorg. Chem. 2000, 39, 4688.