Effect of Different Concentrations of Mineralization Agent on the Synthesis of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x=0.05, 0.1, 0.15$)

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Abstract. The $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x = 0.05, 0.1, 0.15$) diluted magnetic semiconductor powders were prepared by hydrothermal synthesis at 220 °C heated for 24 h using NaOH of 3 mol/L and 5 mol/L as the mineralization agent. It is shown that there had a direct relationship between mineralizer concentration and hydrothermal synthesis, pure $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ and $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$ crystal could be prepared using NaOH of 3 mol/L, however, the magnetic features of $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$ crystal is so much better than $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ crystal, which is presented ferromagnetic. Pure $\text{Zn}_{0.85}\text{Mn}_{0.15}\text{O}$ crystal can be synthesized under the condition of 5 mol/L, and the crystal appeared ferromagnetic at room temperature. which indicates that the increase of the concentration of the mineralized agent is beneficial to the doping synthesis.

Introduction

Diluted magnetic semiconductor (DMS) is a new kind of functional material which could produce the magnetic using the carrier control technology, based on nonmagnetic semiconductor materials doped with magnetic ions (such as II-VI, IV-VI, II-V or III-V). Diluted magnetic semiconductor has both properties of the electronic spin and charge free degree, making it have very important significance whether in theory or in application. In recent years, it has been a hot spot research in the field of spin electronics[1-3]. It has been widely studied about the diluted magnetic semiconductor material which is doped with transition metal elements using zinc oxide as matrix. Diet et al^[1] predicted that $\text{Mn}_{1-x}\text{Zn}_x\text{O}$ had ferromagnetism at room temperature by calculating when the Mn content was less than 5%, and the hole concentration reached $3.5 \times 10^{20}/\text{cm}^3$, which made people pay attention to the ZnO diluted magnetic semiconductor. Ando et al[2] reported that ZnO doped with Mn, Co, Ni, Cu could have a ferromagnetic function due to the presence of sp-d electron magnetic exchange using magnetic circular dichroism method. Sato et al [3,4] inferred that ZnO doped with Fe, Co, Ni could create ferromagnetic properties by the theoretical calculation.

Curie temperature depends on the competition between the ferromagnetic and anti ferromagnetic interactions for a given material with certain content of Mn and hole density because that the interaction between the Mn-Mn is anti ferromagnetic. (In,Mn)As and (Ga,Mn)As ferromagnetic semiconductors[5] were prepared by the magnetic ions instead of positive ions in the non magnetic semiconductors, however, the Curie temperature(T_c) is 173 K and 61 K respectively, which were far below 300 K at room temperature [6,7]. And so, the transition metal doped ZnO has become the most widely studied material. ZnO is a direct band gap semiconductor with bandwidth of $E_g=3.36$, which could change by doping in the position of the cations due to its bandwidth. Some experiments have been reported on Fe, Mn, Co, Ni doped ZnO [8-13], At present, some research groups have carried on the preliminary research on the ZnO doped with Mn. $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ [14] nano powder had a room temperature ferromagnetic, while the annealed samples in the air had a paramagnetic.

There are many methods for preparing ZnO diluted magnetic semiconductor materials according to the present reports, such as solid phase reaction method, molecular beam epitaxy, etc, which are also a kind of non-equilibrium doping method, easily to form a non-uniform phase and the impurity phase,

leading people have many questions about the synthesis of diluted magnetic semiconductor [15-21]. Hydrothermal method is one of the equilibrium doping method, which could obtain crystal with uniform doping, lower heat stress, small force, less defects and better quality. In this paper, $Zn_{1-x}Mn_xO$ nanocrystals were synthesized by hydrothermal method, and their magnetic properties were studied.

Experimental

$Zn_{1-x}Mn_xO$ ($x=0.05, 0.10, 0.15$) diluted magnetic semiconductor powder using NaOH as mineralization agent with 24 hours of heat preservation. All reagents were not further purified displayed in Table 1. Teflon lining autoclaves of 40 ml were used and two series of samples had been synthesized with hydrothermal method as reported in Table 2.

Table 1 Reagent medicine used in the experiment

Reagent	Purity	Content	Molecular weight
$Zn(CH_3COO)_2 \cdot 2H_2O$	AR	$\geq 99.0\%$	219.50
$Mn(CH_3COO)_2 \cdot 4H_2O$	AR	$\geq 99.0\%$	245.09
NaOH	AR	$\geq 96.0\%$	40.00
CH_3CH_2OH	AR	$\geq 99.5\%$	46.07
$(C_2H_4O)_n$	AR	—	$(44.05)_n$

Table 2 Two groups of experimental design conditions

Series	$Zn_{1-x}Mn_xO$	[NaOH] (mol/L)	Reaction Temperature ($^{\circ}C$)
1	$x=0.05, 0.10, 0.15$	3	240
2	$x=0.15$	5	240

The structural analysis of the as-prepared powders was shown through X-ray diffraction (XRD, D/max-200PC, RIGAKU, Japan) collecting in the 2θ range from 15° to 70° . The magnetic properties were tested at room temperature using vibrating sample magnetometer (VSM, 7303, LakeShore, America). And the microstructures of the powders were displayed by a field emission scanning electron microscopy (FE-SEM, JSM-6700F, JEOL, Japan).

Results and Discussion

Fig.1. XRD spectras of as-synthesized $Zn_{1-x}Mn_xO$ ($x=0.05, 0.10, 0.15$) crystal powders

Fig. 2. XRD spectras of as-synthesized $Zn_{0.85}Mn_{0.15}O$ crystal powders using NaOH of 3mol/L and 5mol/L as mineralization agent

Fig. 1 shows the XRD patterns of the $Zn_{1-x}Mn_xO$ powder produced by the doping amount of $x = 0.05, 0.10, 0.15$, which displays that the obtained $Zn_{1-x}Mn_xO$ powder has pure phase structure of $x = 0.05, 0.10$ without additional peaks, while the impurity phase MnO_2 appears with the content of $x =$

0.15. In the light of the impurity phase during the process of preparing $\text{Zn}_{0.85}\text{Mn}_{0.15}\text{O}$ powder, concentration of mineralization agent is improved to 5 mol/L, as shown in Fig. 2, the impurities would disappear along with the increase of the concentration of the mineralized agent, the result shows that the high concentration of the mineralized agent is beneficial to Mn^{2+} doping ZnO.

The particle morphology of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ ($x=0.05, 0.10, 0.15$) powders were obtained by field emission scanning electron microscope (SEM) in Fig. 3, where the picture (a) is 5000 times showing a square shape, the picture (b) is enlarged 10000 times and (c) is the 20000 multiples of the picture, presenting in granular form mostly. The particle size decreases with the increase of the doping concentration and the concentration of the mineralization agent.

Fig. 3. SEM images of $\text{Zn}_{1-x}\text{Mn}_x\text{O}$ crystal powders of (a) $x=0.05$, (b) $x=0.10$, (c) $x=0.15$

Fig.4. Magnetic energy curve of the as-prepared crystal powders at room temperature:(a) $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$, (b) $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$ and (c) $\text{Zn}_{0.85}\text{Mn}_{0.15}\text{O}$.

After the magnetic test, $\text{Zn}_{0.95}\text{Mn}_{0.05}\text{O}$ crystal is not appear rule of magnetic energy change curve as shown in Fig. 4(a). while the magnetic energy curves of $\text{Zn}_{0.9}\text{Mn}_{0.1}\text{O}$ and $\text{Zn}_{0.85}\text{Mn}_{0.15}\text{O}$ crystals are regular, and the ferromagnetic properties is also present at room temperature in Fig. 4(b) and Fig. 4(c), which displayed that the magnetic properties is relatively to Mn doping content, so it is observed that how to improve the yield of the doping concent. According to forming conditions of substitutional solid solution,

$$X = \left| \frac{R_1 - R_2}{R_1} \right|$$

where R_1 is the Zn^{2+} radius of 0.083 nm, R_2 is Mn^{2+} radius of 0.067 nm, respectively. The ratio of two ion radius X can be calculated as 19.3%, which is between 15% ~ 30% indicating that Mn ions could enter the crystal lattice and instead of Zn ions forming finite substitutional solid solution. It is generally believed that ferromagnetic property is originated from ion implantation or the defect. And so the ferromagnetic of $Zn_{0.9}Mn_{0.1}O$ and $Zn_{0.85}Mn_{0.15}O$ crystals should come from the Mn ion doping, however, $Zn_{0.95}Mn_{0.05}O$ crystal is not appear good magnetic, which may be caused by crystal defects.

Conclusions

There is a direct relationship between mineralization concentration and hydrothermal synthesis. Pure $Zn_{0.95}Mn_{0.05}O$ and $Zn_{0.9}Mn_{0.1}O$ crystals can be synthesized using NaOH of 3 mol/L, while $Zn_{0.85}Mn_{0.15}O$ can be synthesized under the condition NaOH of 5 mol/L, which indicates that increasing the concentration of the mineralized agent is helpful to the doping. From the view of magnetic, the magnetic property of $Zn_{0.95}Mn_{0.05}O$ crystals is irregular, however, $Zn_{0.9}Mn_{0.1}O$ and $Zn_{0.85}Mn_{0.15}O$ crystals show ferromagnetic. at room temperature, which shows that doping concent is also important.

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