Volume 9, Number 9
1009-1963/2000/09(09)/0685-04
CHINESE PHYSICS
September, 2000
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STRUCTURE AND MÖSSBAUER STUDY OF NANOCRYSTALLINE Ni-Zn FERRITE*

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(Received 3 January 2000)

$Ni_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 1.0$) nanoparticles have been prepared by the polyvinyl alcohol (PVA) sol-gel method. The lattice parameter of Ni-Zn ferrite nanoparticles is larger than that of the bulk material. The variation of saturation magnetization (M_s) as a function of x has been studied. The Mössbauer spectra of the samples at room temperature showed the presence of ultrafine particles, exhibiting superparamagnetic relaxation. At higher annealing temperature, the portion of the ferromagnetic ultrafine particles increased.

Keywords: Ni-Zn ferrite, nanosized particle, Mössbauer spectra
PACC: 7650, 7570K

I. INTRODUCTION

Ni-Zn ferrite is a group of technologically important materials, synthetized for the first time about 50 years ago. It has been studied extensively.[1,2] They have been commercially used as high-frequency ferrite for radio frequency coils, transformer cores,[3,4] prepared by the conventional ceramic method at high temperatures, which can result in the loss of their fine particle nature.[1,2] Recently, research of nanocrystalline materials and their properties has been received much attention. Wet chemical methods such as co-precipitation, hydrothermal oxidation have been used to yield Ni-Zn ferrite particles with size ranging from 10 to 100nm.[5−13] It has been shown that the properties of materials composed of nanocrystalline particles are drastically altered when compared to their bulk counterparts. There is a specialized application of Ni-Zn ferrite, which requires low porsity and controlled microstructure. We have tried to prepare nanosized Ni-Zn ferrite particle at low temperature by sol-gel method, to investigate the crystal structure, magnetic properties of it.

II. EXPERIMENTAL

Ni, Zn and Fe nitrates were dissolved together in a minimum amount of deionized water, to produce a clear solution. Polyvinyl alcohol (PVA) was used to make a gel. The aqueous PVA solution were added to the nitrate solution and dehydrated at 60–80°C. The gelation proceeded step by step and a slightly red gel-type precursor was obtained. The precursor was calcined at different temperatures to obtain $Ni_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 1.0$) fine powders with size ranging from 6 to 90nm.

The crystalline structure was investigated by X-ray diffraction (XRD). Magnetization measurements were carried out with a vibrating sample magnetometer (VSM). The Mössbauer spectra of the various samples were recorded in constant acceleration mode. A ^{57}Co radioactive source was used. The spectrometer was caliberated using α-Fe.

III. RESULTS AND DISCUSSION

A. Results of XRD and VSM

The X-ray diffractograms of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ annealed at four different temperatures are shown in Fig.1. It is evident that in all cases the spinel phase could be produced at rather low temperatures compared with the conventional solid-ceramic techniques (1100–1400°C) and the diffraction peaks are fairly broad particulary for the sample annealed at lower temperatures. The crystallite size of the spinel phase has been estimated from the broadening of the XRD peaks using the Scherrer equation.

$$D = \frac{0.9\lambda}{(\beta - \beta_1)\cos\theta}, \tag{1}$$

where D is the grain diameter, β is the half-intensity width of the relavant diffraction peak, β_1 represents

*Project supported by the Cooperative Projects between China and France of the Ministry of Education of China (Grant No. 959, 1997).

the half-intensity width due to instrumental broadening, λ is the X-ray wavelength, and θ is the angle of diffraction. Particle sizes of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ as calculated from Eq.(1) are shown in Table 1. It is evident that the crystallite size of the ferrite phase obtained in the present investigation varies from 6.0 to 50.1nm, depending on the calculation temperature. From Fig.1, it may be noticed that no change in the crystal structure occurs in the XRD patterns of the power. The only effect is that the X-ray line broadening gradually decreases with increasing annealing temperature, which is due to the grain growth of the large crystallites at higher temperatures.

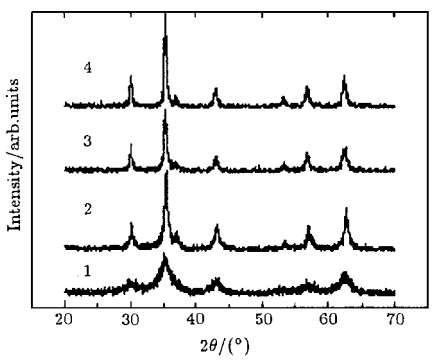


Fig.1. X-ray diffractogram of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ heat-treated at (1)350°C (2)450°C (3)500°C (4)550°C.

Table 1. Particle size of $Ni_{0.5}Zn_{0.5}Fe_2O_4$ heat-treated at different tmperature.

Sample	T/°C	D/nm
1	350	6.0
2	450	23.0
3	500	49.6
4	550	50.1

In addition, the X-ray diffractograms of $Ni_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 1.0$) heat-treated at 450°C show that the spinel nanosized particle could be produced in all cases. The lattice constants of the nanosized $Ni_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 1.0$) are compared with that of the bulk material in Fig.2. The apparent variation of lattice constant with x is in agreement with previously obtained results.[14,15] But the lattice constant of Ni-Zn ferrite nanoparticle is 0.2% larger than that of the bulk material. It may be caused by the small particle size and the interface structure with a large volume fraction.[16] It was found in other nanocrystallite before,[17] but it is the first time to find in Ni-Zn ferrite nanoparticle.

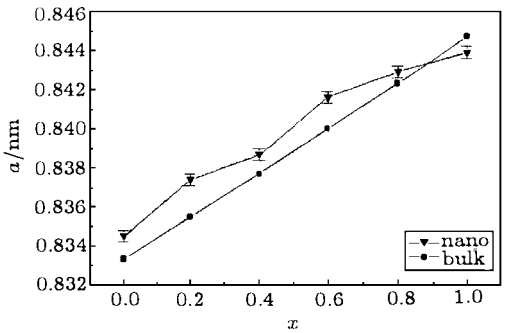


Fig.2. Variation of lattice constant as a function of x in $Ni_{1-x}Zn_xFe_2O_4$.

The variation of saturation magnetization with zinc concertration is given in Fig.3, which is in agreement with previously obtained results of the bulk material.[14] But the magnetization curves of Ni-Zn ferrite at room temperature showed no hysteresis, indicating that the ferrites are superparamagnetic at room temperature, which is confirmed in Mössbauer spectra.

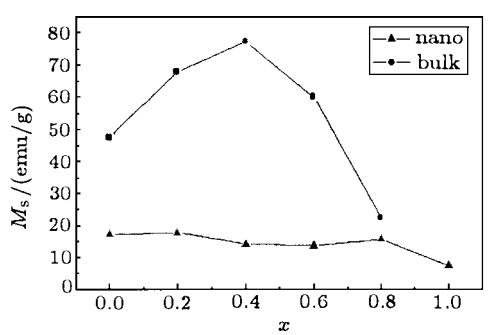


Fig.3. Variation of suturation magnetization as function of x in $Ni_{1-x}Zn_xFe_2O_4$.

B. Mössbauer spectra

Figure 4 shows the Mössbauer spectra taken at room temperature for $Ni_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 1.0$) heat-treated at 350°C. It exhibites clear doublet and superparamagnetic relaxation for different x. The points represent the experimental results and the continuous line corresponds to computer fitting data, which are listed in Table 2.

Table 2. Results of Mössbauer effect measurements on $Ni_{1-x}Zn_xFe_2O_4$. $\overline{IS}$ is the average isomer shift, $\overline{QS}$ the average quadrupole splitting.

x	0.0	0.2	0.4	0.5	0.6	0.8	1.0
$\overline{IS}$/(mm/s)	0.15	0.15	0.15	0.16	0.15	0.16	0.16
$\overline{QS}$/(mm/s)	0.78	0.64	0.65	0.62	0.65	0.61	0.61

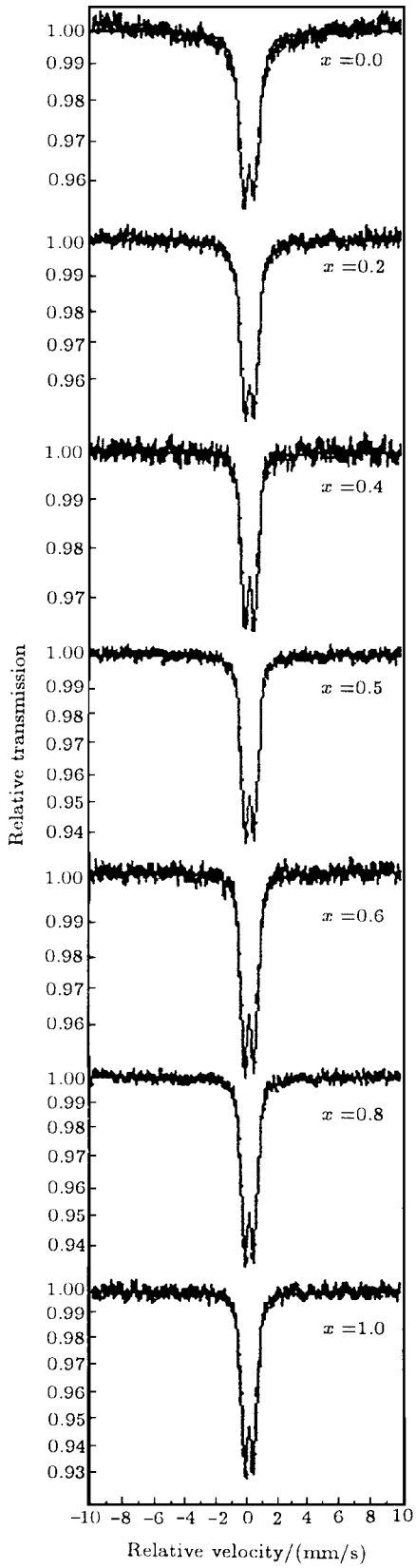


Fig.4. Mössbauer spectra of $Ni_{1-x}Zn_xFe_2O_4$ at room temperature.

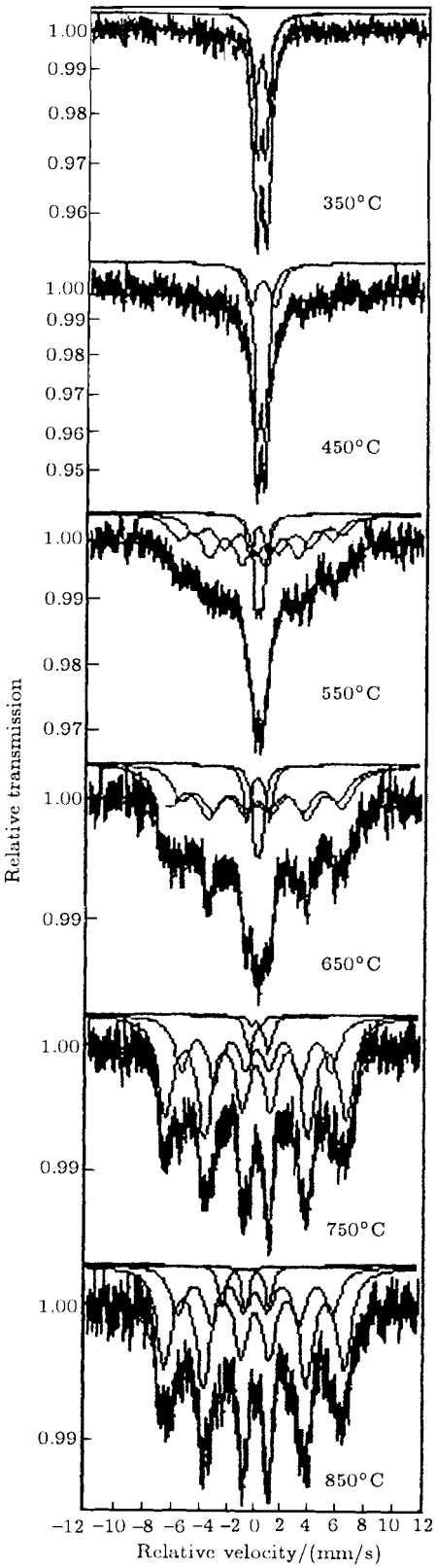


Fig.5. Mössbauer spectra of $Ni_{1-x}Zn_xFe_2O_4$(x=0.6) heat-treated at different temperatures.

We note that the average isomer shifts $\overline{IS}$ of $Ni_{1-x}Zn_xFe_2O_4$ appear to show no significant variation with x, indicating that the s-electron charge distribution of Fe^{3+} ions is negligibly influenced by Zn substitution. This result agrees with the obtained result of the bulk material in 1970 by Daniels.[14] But the average quadrupole splitting $\overline{QS}$ of nanosized Ni-Zn ferrite particle is larger than that of the bulk material,[14] for example, the $\overline{QS}$ of $ZnFe_2O_4$(x=0.0), is 0.32 mm/s in the bulk material, but 0.78 mm/s in nanosized particle. This indicates that there is difference in the structure between the nanosized material and the bulk material. Large lattice strain results in noncubic symmetry, and the increase of lattice constant (XRD) results in the increase of the electric field gradient(or EFG) at a ^{57}Fe nucleus. These can all result in the increase of $\overline{QS}$.

Figure 5 shows the Mössbauer spectra taken at room temperature for $Ni_{1-x}Zn_xFe_2O_4$(x=0.6) annealed at different temperatures. The Mössbauer spectra of the samples annealed at low temperatures exhibite superparamagnetic doublet, but the spectra of the samples annealed at higher temperatures exhibite sextets. The high temperature annealing changes the ultrafine particle ferrite into the ordered magnetic structure, because the average size of the particles increases, extreme lattice strain is reduced with increasing annealing temperature.

IV. CONCLUSIONS

The sol-gel technique has been used to prepare $Ni_{1-x}Zn_xFe_2O_4$ particles of nanometre dimensions. By using a suitable heat treatment procedure it is possible to obtain ferrite particles of sizes varying from 6 to 90nm. The saturation magnetization of the nanosized particles is lower than that of the bulk material. Mössbauer spectra of samples confirm the presence of superparamagnetic particles at room temperature. By high temperature annealing, the particle size increases, then magnetic sixtets appear.

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