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Structural and magnetic properties of $Co_{1-x}Zn_xFe_2O_4$ nanoparticles

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$Co_{1-x}Zn_xFe_2O_4$ nanoparticles, prepared by the polyvinyl alcohol sol–gel method, have been investigated by x-ray diffraction and Mössbauer spectroscopy. These results are compared with those for the bulk material. The lattice parameters of CoZn ferrite nanoparticles are larger than those of the bulk material. Thermal scanning of Mössbauer measurement shows that the transition temperatures for nanoparticles are higher than those of the bulk material except for the sample $CoFe_2O_4$.

Keywords: ferrite, nanoparticle, Mössbauer spectra
PACC: 6146, 7590, 7680

1. Introduction

Spinel ferrites are a commercially important material because of their excellent magnetic and electrical properties.[1] The usefulness of ferrites is restricted by the physical and chemical properties of the materials. In recent years, nanosized spinel ferrite particles have attracted considerable attention, for their variations of physical and chemical properties are markedly different from those of their bulk counterparts.[2,3]

Many synthetic approaches to preparing magnetic nanocrystals have been suggested, such as co-precipitation, hydrothermal oxidation and sol–gel method.[4−7] $CoFe_2O_4$ is increasingly arousing the interest in research because of its potential applications in nanoscience and technology.[8,9] Non-magnetic Zn doped Co ferrites are of interest in a fundamental understanding of the properties. However, not much attention has been paid to the investigation of the properties of the nanosized $Co_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 1.0$). In this article, we prepare nanosized CoZn ferrite particles for the values of x ranging from 0.0 to 1.0 in steps of 0.1 by using the sol–gel method. Thereafter, the crystal structure and the magnetic properties of the particles are investigated. Thermal scanning of Mössbauer spectroscopy is used to measure the magnetic ordering temperatures for the particles.

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2. Experiments

A mixture of Co, Zn and Fe nitrates with an appropriate ratio was dissolved together in a minimal amount of deionized water to produce a clear solution. Polyvinyl alcohol (PVA) was added to form a gel. The aqueous PVA solution was mixed with 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 heated at 800°C to obtain CoZn ferrite fine particles.

The crystalline structure was investigated by x-ray diffraction (XRD). Magnetization measurements were carried out with a vibrating sample magnetometer (VSM) at room temperature. Thermal scanning was recorded by Mössbauer spectroscopy from 300K to 873K. A ^{57}Co radioactive source was used.

3. Results and discussion

The x-ray diffractograms of $Co_{1-x}Zn_xFe_2O_4$ with x=0.0 and 1.0, annealed at 800°C, are shown in Fig.1. It is evident that the spinel phase could be produced at rather low temperatures compared with those by using the conventional solid-ceramic techniques (1100–1400°C). The crystallite size of the nanoparticles has been estimated from the broadening of the XRD peaks

from the Scherrer equation as follows:[10]

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

where D is the grain diameter, β is the full width at half maximum (FWHM) of the relevant diffraction peak, β_1 represents the FWHM due to instrumental broadening, λ is the x-ray wavelength, and θ the diffraction angle. The average size of nanoparticles is about 35nm.

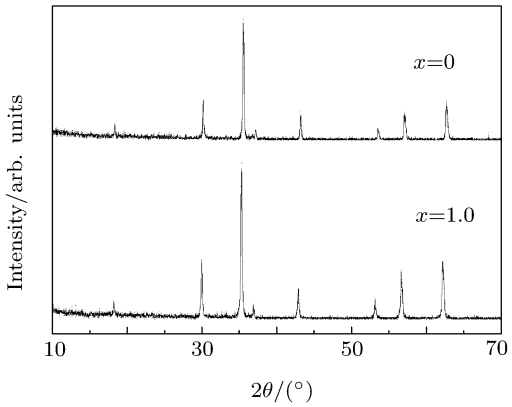


Fig.1. The x-ray diffractograms of $Co_{1-x}Zn_xFe_2O_4$, x=0.0 and 1.0, annealed at 800°C.

In addition, the x-ray diffractograms of $Co_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 1.0$) heat-treated at 800°C are show that the spinel nanosized particle can be produced in all cases. The lattice constants of the nanosized $Co_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 1.0$) are compared with those of bulk material in Fig.2. In many substitutional solutions the lattice parameter is a linear function of solute concentration with either a negative or a positive slope, called Vegard's law, over a range of concentrations. A linear change in the lattice constant of bulk $Co_{1-x}Zn_xFe_2O_4$ with the zinc concentration was observed.[11] The lattice parameters of CoZn ferrite, which was synthesized by the microwave-hydrothermal method, increased linearly with the increase of Zn content, which suggested the formation of a compositionally homogeneous solid solution.[12] Non-linear behaviour for our system is unusual. The strain energy, the stress field, the compressibilities of the components and the free electron-gas concept could result in the deviations from Vegard's law.[13] According to Ref.[14], the deviation from Vegard's law is caused by relevant defects. The nanoparticles may involve lattice deformation, lattice defect, oxygen vacancy and local disorder,[15,16] spin canting[17] of which all may affect the ions in the spinel structure deviating from their equilibrium position, changing both the bond angle and bond length. On the other hand, the lattice constants of CoZn ferrite nanoparticles are larger than those of the bulk material. It may be caused by the small particle size and the interface structure with a large volume fraction.[18] It has been found in NiZn ferrite nanoparticles before,[19] but it is the first time that it has been found in CoZn ferrite nanoparticles.

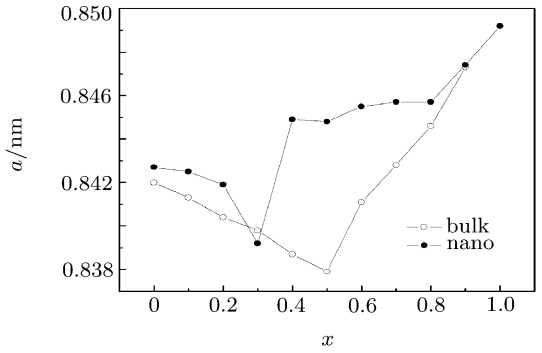


Fig.2. Lattice constant a versus zinc concentration x for nanoparticle-type and bulk $Co_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 1.0$).

The variation of saturation magnetization with x is given in Fig.3. The initial increase is attributed to the preferential occupation of A sites by Zn^{2+}, thus displacing Fe^{3+} from A sites to B sites,[20] leading to the difference in magnetization between the A sublattice and the B sublattice in the antiferromagnetic coupling. For $x > 0.4$ samples, the variation of Ms with zinc concentration can be explained on the basis of Yafet–Kittel type of spin arrangement.[21] With the zinc concentration increasing, the Fe^{3+} ions have no magnetic neighbours and hence spins become uncoupled, and the saturation magnetization decreases. This is confirmed in Mössbauer spectra.

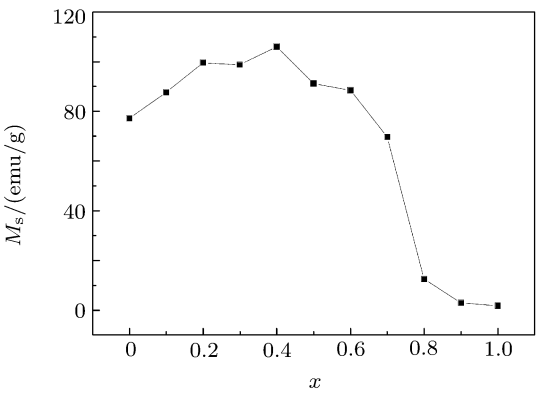


Fig.3. The variation of saturation magnetization with zinc concentration x.

Mössbauer spectroscopy is a powerful tool for determining the transition temperature as well as examining the distribution of metal cations on the various crystal sites. In Mössbauer measurements, thermal scanning is an efficient tool to determine the transition temperature. As is known, when the phase transition happens, the spectrum changes dramatically from a well-defined sextet to a single central peak as temperature increases. That means that the counts of some channels will change dramatically. Therefore instead of recording all the Mössbauer spectra at each temperature, we fixed on a certain channel of Mössbauer spectroscopy and took the counts of this channel with the variation of temperature. According to the variation of the counts, the transition temperatures of the samples are found. In our experiment, temperature of thermal scanning from 300 to 873K. The transition temperature T_c of $Co_{1-x}Zn_xFe_2O_4$ ($0.1 \leq x \leq 1.0$) is shown in Table 1 and compared with that of bulk material.[20]

Table 1. The transition temperature T_c of $Co_{1-x}Zn_xFe_2O_4$ ($0.1 \leq x \leq 1.0$).

x	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9	1.0
T_c/K bulk	860		700		540		360		180		10
T_c/K nano	803 ±10	793 ±10	823 ±10	753 ±10	693±10	653 ±10	513 ±10	463 ±10	300 ±10		

Figure 4 gives the variation of the transition temperature T_c with zinc concentration x. The T_c of the nanoparticles is higher than that of the bulk sample except for the sample with x=0.0.

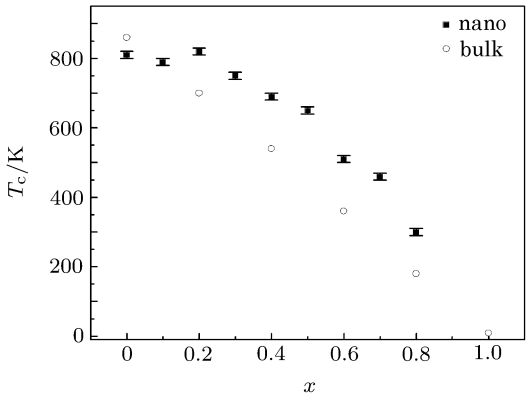


Fig.4. The variation of the transition temperature T_c with zinc concentration x.

It is well known that there are two sites, A (tetragonal) and B (octahedral), in the spinel ferrite MFe_2O_4. The general formula can be written as $M_\delta Fe_{1-\delta}[M_{1-\delta}Fe_{1+\delta}]O_4$,[22] where the cations on B sites are indicated in brackets and δ is the inversion parameter. Note that, the extreme case, $\delta = 1$ is a normal spinel. A typical example is bulk $ZnFe_2O_4$ in which the divalent cations, Zn^{2+}, occupy A sites only (while Fe^{3+} cations occupy B sites). The other extreme case, $\delta = 0$ is a complete inverse spinel. Typical examples are $CoFe_2O_4$ in which divalent cations of Co and Fe occupy the B sites. Superexchange interactions between the two metal cations via an intermediate oxygen ion in the spinel structure can occur as a result of intra-sublattice AA and BB interactions and inter-sublattice AB interactions.

Usually, the transition temperature of the spinel ferrite depends on the strength of all three superexchange interactions. Among them A–B is the strongest one and A–A is the weakest one.[23] $CoFe_2O_4$ (x=0.0) nanoparticle prepared by sol–gel method may be not a complete inverse spinel. The Fe^{3+} ions at the A-sites migrate to the B-sites, which weakens the A–B superexchange interactions. The origin for the decrease in the T_c of $CoFe_2O_4$ (x=0.0) nanoparticles is far more likely attributable to the redistributions of Fe and Zn cations on the A and B sites. $Co_{1-x}Zn_xFe_2O_4$ ($0.1 \leq x \leq 1.0$) is not homogeneous as a bulk material. Fe cations of nanosized $Co_{1-x}Zn_xFe_2O_4$ particles are redistributed on the A and the B sites, which will increase T_c. The similar result about $ZnFe_2O_4$ nanosized particles has been found before.[24] Furthermore, the transition occurring over a wider temperature range about 20K is considered as a result of size distribution in nanoparticles.

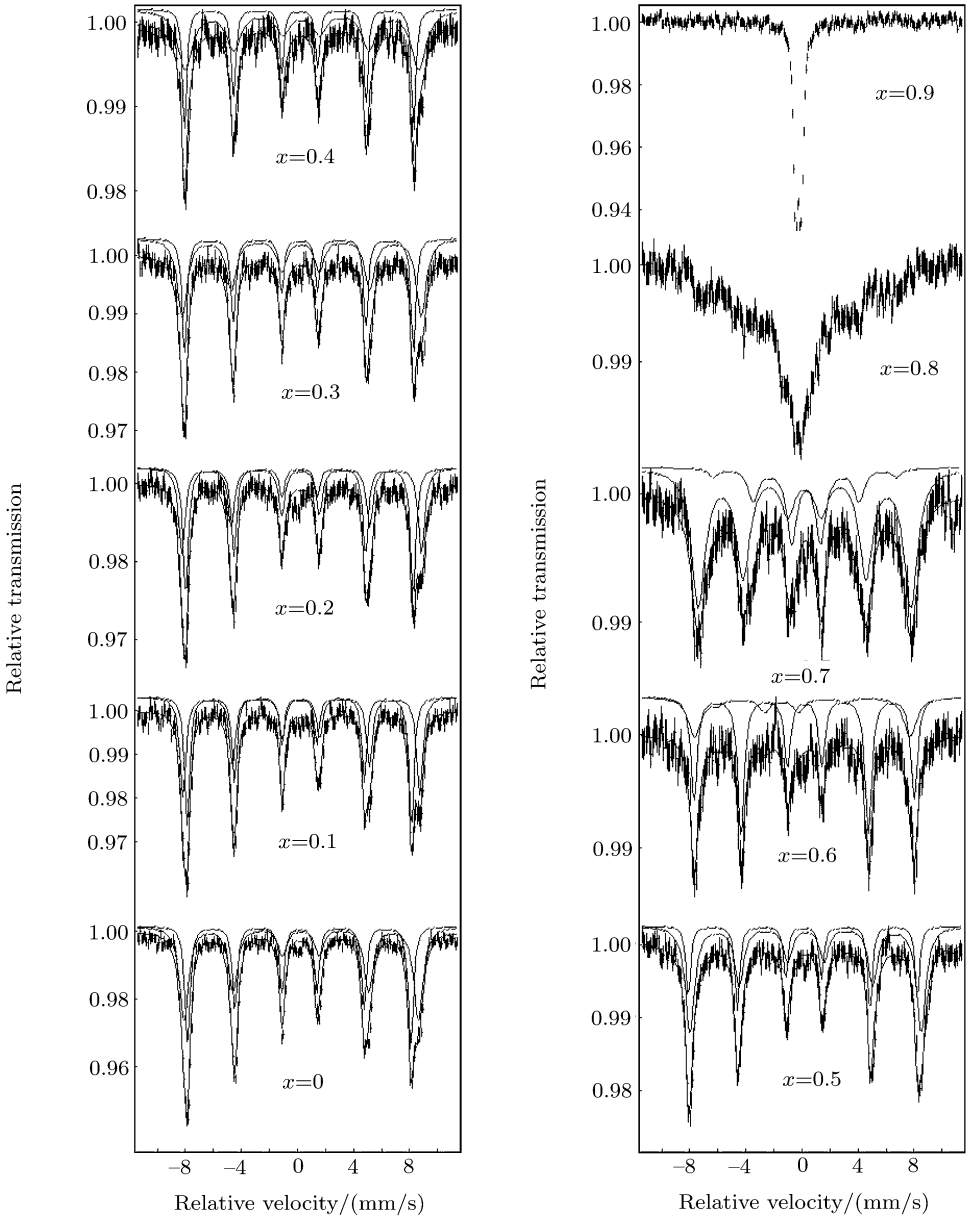


Fig.5. Mössbauer spectra of $Co_{1-x}Zn_xFe_2O_4$ taken at 80K

Figure 5 shows the Mössbauer spectra taken at 80K for nanosized $Co_{1-x}Zn_xFe_2O_4$ ($0.0 \leq x \leq 1.0$). The points represent the experimental results and the continuous line corresponds to computer fitted data. Fitted data about the variation of average hyperfine field $\overline{H_f}$ with zinc concentration x is given in Fig 6. The apparent variation of $\overline{H_f}$ accords with the variation of Ms. As the increase of zinc concentration, the saturation magnetization decreases, and hence the hyperfine field decreases.

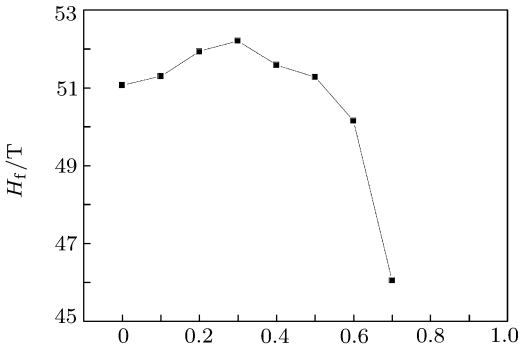


Fig.6. The variation of average hyperfine field $\overline{H_f}$ with zinc concentration x.

4. Conclusions

The sol–gel technique has been used to prepare $Co_{1-x}Zn_xFe_2O_4$ particle of nanometre dimensions. At a suitable heat treatment 800°C it has been possible to obtain spinel ferrite in all cases. The lattice parameters of CoZn ferrite nanoparticles are larger than those of the bulk material. Thermal scanning of Mössbauer measurement shows that the transition temperatures for particles are higher than those of the bulk material. With the increase of zinc concentration, the saturation magnetization decreases, and hence the hyperfine field decreases.

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