Physica B 405 (2010) 4211–4215

Contents lists available at ScienceDirect

Physica B

journal homepage: www.elsevier.com/locate/physb

Effect of particle size on degree of inversion in ferrites investigated by Mössbauer spectroscopy

M. Siddique [a,*], N.M. Butt [b]

[a] Physics Division, PINSTECH, P.O. Nilore, Islamabad, Pakistan
[b] Preston Institute of Science and Technology (PINSAT), Preston University, H-8/1, Islamabad, Pakistan

ARTICLE INFO

Article history:
Received 18 May 2010
Received in revised form
7 July 2010
Accepted 7 July 2010

Keywords:
Ceramics
Magnetic materials
Mössbauer spectroscopy
Nanoparticles

ABSTRACT

Mössbauer spectroscopy has been employed to investigate the cation distribution and degree of inversion in bulk and nanosized particles of $CuFe_2O_4$, $MnFe_2O_4$ and $NiFe_2O_4$ ferrites. The Mössbauer spectra of all bulk ferrites show the complete magnetic behaviour, whereas nanoparticle ferrites are combination of ferromagnetic and superparamagnetic components. Moreover, the cation distribution in nanoparticle materials is also found to be different to that of their bulk counterparts indicating the particle size dependency. The inversion of Cu and Ni ions in bulk sample is greater than that of nanoparticles, whereas the inversion of Mn ions is less in bulk material as compared to the nanoparticles. Hence the degree of inversion (λ) decreases in $CuFe_2O_4$ and $NiFe_2O_4$ samples, whereas it increases in $MnFe_2O_4$ as the particle size decreases and thus shows the anomalous behaviour in this case. The nanoparticle samples also show paramagnetic behaviour due to superparamagnetism and this effect is more prominent in $MnFe_2O_4$.

1. Introduction

Ferrites with the spinel structure are important materials because of their structural, magnetic and electrical properties. The suitability of these materials depends on both the intrinsic behaviour of the material and the effects of the grain size. The capability of producing ultrafine nanosized ferrite powders is important for tailoring the geometry and properties of magnets produced by powder metallurgical processes and are expected to result in new applications due to improved unique properties of these magnetic materials [1]. In recent years nanosized ferrites have been found to have technological desirable magnetic properties relative to ferrites synthesized by traditional routes [2]. The surface effects, in addition to changes in the degree of inversion, cause the nanoferrites to display novel magnetic behaviour [3–6]. Furthermore, the nanosized spinel type ferrites are considered to be the key materials for advancement in electronics, magnetic data-storage (memory), ferrofluid technology and many bioinspired applications [7,8].

Copper ferrite, $CuFe_2O_4$, crystallizes either in a tetragonal or cubic symmetry depending on the cation distribution among the lattice sites of its spinel structure. Superparamagnetic manganese spinel ferrite, $MnFe_2O_4$, nanoparticles have a lot of potentials for technological applications due to their high magnetization and low blocking temperature. Hu et al. [9] have investigated the $MnFe_2O_4$ nanoparticles for the removal and recovery of Cr (VI) from synthetic wastewater. Mn^{2+} cation in spinel is at its high spin state. Its five d electron configurations are $e^2t_2^3$ and $t_{2g}^3e_g^2$ at the tetrahedral and octahedral lattice site, respectively [10]. $NiFe_2O_4$ ferrite is generally assumed to be a completely inverse spinel which finds a number of applications in heterogeneous catalysis and magnetic technologies. It is soft magnetic material having a Neel-type collinear spin arrangement of $(Fe^{3+}\uparrow)[Ni^{2+}\downarrow Fe^{3+}\downarrow]O_4$ [11].

Mössbauer spectroscopy is a very useful and sensitive technique to determine the cation distribution and the spin structure to study the supertransferred hyperfine interactions in the spinel ferrites. These interactions can sense minute changes in the local crystalline structure and magnetic properties of the system [12–14]. The type of cations and their distribution between the two lattice sites in these ferrites determine many of the intrinsic magnetic properties. Interestingly, nanocrystalline spinel ferrites show different cation distribution and, as a consequence, diverse magnetic properties are observed when compared with their bulk counterparts [15,16]. The equilibrium distribution of cations in spinel structure depends on the ionic radii, electronic configuration, electrostatic energies and polarization effects. Nonequilibrium cation distributions are possible using novel or nonequilibrium processing routes. A nonequilibrium distribution of cations in the spinel structure can influence the intrinsic magnetic properties of these materials [17].

Both bulk and nanosized ferrites have significant importance to study because of their numerous applications in all disciplines of science and technology. Furthermore, the comparison of both

* Corresponding author. Tel.: +92 51 2207241; fax: +92 51 9290275.
E-mail address: siddique56@hotmail.com (M. Siddique).

0921-4526/$ - see front matter © 2010 Elsevier B.V. All rights reserved.
doi:10.1016/j.physb.2010.07.012

types of material is also important due to their particle size dependency of the required properties. In the present study we have discussed the Mössbauer parameters, the cations distribution and the degree of inversion in bulk and nanoparticle ferrites and compared them with other workers with reference to their particle sizes. We hope that this study will be useful for the scientific community working in this field.

2. Experimental

Bulk ferrites were prepared in the polycrystalline form by a high temperature solid-state reaction method. The parent oxides NiO, MnO, CuO and Fe_2O_3 (all 99.9% pure) were heated at 1000 °C for 50 h with intermittent grinding for making homogenous products and finally heated for 3 h at 1300 °C for the complete chemical reaction. The heat treatment of the samples, contained in alumina crucibles, was carried out in air. The samples were quenched in air and X-ray diffraction patterns were taken for the confirmation of single phase material.

Nanoparticle ferrites were synthesized using chemical co-precipitation method. First, 200 ml of purified, deoxygenated water was bubbled by nitrogen gas for 30 min, and the $Me(NO_3)_2$ (Me=Mn, Cu, Ni) and Fe $(NO_3)_3$ salts with a molar ratio of 1:2 were successively dissolved in ultrapure water with vigorous mechanical stirring. Under the protection of nitrogen gas, the mixture was heated up to 70 °C in a water bath and then 2 M NaOH was added drop wise into the above solution till pH 11 was achieved. To ensure complete growth of the nanoparticle crystals, the reaction was kept at 70 °C for 2 h. After that, the stirrer was turned off and magnetic particles were allowed to settle down gradually. The precipitates were isolated by the external magnetic field and the supernatant was decanted. For obtaining the pure and neutral products, synthesized materials were rinsed with ultrapure water and the rinse was discarded. The rinsing was repeated for a third time and the magnetic nanogel was then freeze-dried. The resulting particles were dispersed into water and ethanol solutions and centrifuged. However, to obtain nanoscale $CuFe_2O_4$ and $NiFe_2O_4$ ferrites subsequent calcinations at 400 °C for 2 h were needed to ensure the complete crystallization process. The dimension of the synthesized materials was examined by transmission electron microscopy (TEM) JEOL-2010 which was found to be in the range 10–30 nm.

Room temperature Mössbauer effect measurements were carried out using a ^{57}Co (Rh-matrix) radiation source in transmission geometry. The data analysis was performed using a computer programme MOS-90 [18], assuming that the peaks were Lorentzian in shape. The quality of data fitting was checked by the χ^2-test.

3. Results and discussion

3.1. $CuFe_2O_4$

$CuFe_2O_4$ can be described as cubic close-packed arrangement of oxygen ions with Cu and Fe^{3+} ions at two crystallographic sites. These sites are tetrahedral (A) and octahedral (B) oxygen coordinated, so the resulting local symmetries of the two sites are different. The cation distribution in this kind of structure may be represented by $(Cu_xFe_{1-x})^A[Cu_{1-x}Fe_{1+x}]^BO_4$, where x is the inversion parameter and $x=0$ and 1 stand for the inverse and normal cases, respectively. Spinels with cation distribution between these two extremes are called partially inverse or mixed spinels. Most of the spinel ferrites are cubic; however, $CuFe_2O_4$ can have also tetragonal unit-cell symmetry if sample is slowly cooled from high temperature.

In the present study bulk material has been prepared in cubic symmetry, which forms mixed spinel structure. This is confirmed from quadrupole splitting, originating from the electric field gradient (i.e. $\Delta\sim0$, given in Table 1). The analysis of Mössbauer spectrum of bulk sample indicates that it comprises two subspectra; one for tetrahedral (A) site and other for octahedral (B) site while in nanosized sample the spectrum constituted four subspectra; one for A-site and three for B-site (see Fig. 1). This means that Fe at B-site has three types of environments at A-site, which are interacting with B-site Fe and cation distribution is more random in nanoparticles than that of bulk material. The cation distribution has been discussed in detail in our earlier studies [19,20].

The magnetic characteristics of the material are strongly affected when the particle size becomes very small, due the influence of thermal energy over the magnetic moment ordering, originating the superparamagnetic relaxation phenomenon [3,21]. To interpret the Mössbauer spectra the superexchange interaction via oxygen ions must be considered. The strength of the interaction decreases as the distance between the magnetic ions increases, and also as the angle of the Fe–O–Fe bonds decreases from 180° to 90°. It is well known that the Fe(A)–O–Fe(B), the A–B interaction, is antiferromagnetic and much

Table 1
Mössbauer parameters of bulk and nanoparticles ferrites.

Sample	H_{eff} (kOe)		Δ (mm/s)		δ (mm/s)		Γ (mm/s)		**Area** (%)	
	Bulk	Nano	Bulk	Nano	Bulk	Nano	Bulk	Nano	Bulk	Nano
$CuFe_2O_4$	**477**	**477**	**−0.02**	**−0.02**	**0.21**	**0.26**	**0.60**	**0.79**	**44**	**40**
	482	503	−0.02	−0.33	0.44	0.37	0.82	0.44	56	15
		409		−0.42		0.36		2.43		18
		–		0.68		0.36		0.74		27
$MnFe_2O_4$	**487**	**455**	**0.08**	**0.24**	**0.13**	**0.34**	**0.26**	**0.88**	**10**	**27**
	474	405	−0.16	0.00	0.34	0.59	0.46	2.20	26	15
	472	–	0.17	0.68	0.37	0.34	0.54	0.52	21	58
	434		−0.12		0.46		0.34		06	
	430		−0.10		0.35		0.78		37	
$NiFe_2O_4$	**493**	**486**	**0.02**	**0.02**	**0.02**	**0.25**	**0.48**	**0.77**	**50**	**43**
	527	519	0.02	−0.10	−0.10	0.36	0.44	0.48	50	29
		437		−0.32	−0.32	0.32		2.45		26
		–		0.20	0.20	0.33		0.33		2

Mössbauer parameters in bold letters are for tetrahedral A-site and others are for octahedral B-sites (B1, B2, B3, …).
All Mössbauer parameters are with reference to α-Fe.