Materials Research Bulletin 59 (2014) 1–5

Contents lists available at ScienceDirect

Materials Research Bulletin

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

Cation distribution in Ni–Cu–Zn nanoferrites from ^{57}Fe in-field Mössbauer spectra

P. Prameela [a], A. Mahesh Kumar [b,*], G.S.V.R.K. Choudary [c], K.H. Rao [b], V.R. Reddy [d]

[a] *Department of Physics, GITAM University, Visakhapatnam 530045, India*
[b] *Department of Physics, RGUKT, IIIT, Nuzvid 521201, India*
[c] *Department of Physics, BVB Vivekanada College, Sainikpuri, Secunderabad 500094, India*
[d] *UGC-DAE-CSR, Indore 452001, India*

ARTICLE INFO

Article history:
Received 6 April 2013
Received in revised form 28 April 2014
Accepted 30 April 2014
Available online 2 May 2014

Keywords:
Sol–gel chemistry
Mössbauer spectroscopy
Cation distribution
Lattice constant
Site occupancy

ABSTRACT

The nanoparticles of $Ni_{1-x}Cu_xZn_{0.35}Fe_2O_4$ were synthesized by sol–gel method using polyvinyl alcohol as a chelating agent. X-ray diffraction patterns of all the samples confirmed the single phase spinel structure. The site occupancy of copper in the nanosized nickel–zinc ferrite spinels was investigated with the help of in-field Mössbauer spectroscopy. Cation distribution for the whole series of compositions was proposed by considering the amounts of iron ions present at both tetrahedral and octahedral interstitial sites in the spinel lattice. Confirmation of the proposed distributions was done by estimating quantitatively the lattice parameters for these compositions and comparing their values with those of the experimentally observed ones.

© 2014 Published by Elsevier Ltd.

1. Introduction

The extensive study of numerous researchers on mixed ferrite systems has revealed that Ni–Zn bulk ferrite was the only core material useful for high frequency applications due to its high saturation magnetization and dc resistivity. The usefulness of the nickel–zinc ferrite at far high frequencies can be expected if saturation magnetization and dc resistivity are further improved. It is well known that the properties of nanophase ferrites strongly depend on the particle size, cation distribution, and synthesis route. Careful annealing of the nanosized $Ni_{0.65}Zn_{0.35}Fe_2O_4$ sample synthesized by sol–gel method appreciably improves the saturation magnetization and dc resistivity [1]. This improvement has been attributed to the vast number of fine grains of optimum size and grain boundaries formed at lower sintering temperature. It has been shown that the addition of CuO also lower its sintering temperature of bulk Ni–Zn ferrite [2,3].

Copper substituted Ni–Zn bulk ferrites have been found to be better materials for multilayered chip inductors (MLCI) due to their high permeability, high quality factor, high saturation magnetization and high dc resistivity. Although some researchers [4–6] have made attempts to improve the desired characteristics of Ni–Cu–Zn ferrites, the intended progress to make use of them for MLCI applications is not up to expected level. The amount of the copper content present in the ferrite and its distribution among both the tetrahedral (A) and octahedral (B) sites of the ferrite lattice would provide useful information for the improvement of essential properties. Several contradictory opinions have been reported [7–13] on the site occupancy of copper ions in nickel–zinc ferrites. According to some researchers, copper ions prefer to occupy either B-sites [7–9] or A-sites [10,11] exclusively, while in some reports copper ions have been found to occupy both the A and B-sites [12,13]. A thorough understanding of the distribution of cations and the dependent parameters would permit to develop good materials for suitable applications.

In this article, we will report significant information about the distribution of copper ions in Ni–Zn nanoferrites, using X-ray diffraction and ^{57}Fe in-field Mössbauer measurements.

2. Experimental

The detailed description about the processing of the $Ni_{1-x}Cu_xZn_{0.35}Fe_2O_4$ ($x = 0.00$–0.30 in steps of 0.06) has been reported elsewhere [1]. ^{57}Fe Mössbauer spectra have been recorded for the Ni–Cu–Zn ferrites at 5 K and in the presence of an external magnetic field of 5 T at 5 K oriented parallel to the γ-radiation and the Mössbauer parameters are obtained from the NORMOS fitting program. Isomer shift (δ) with respect to Co^{57}: Rh, linewidth (Γ),

---

[*] Corresponding author. Tel.: +91 9618188768.
E-mail address: drmaheshnano@gmail.com (A. M. Kumar).

http://dx.doi.org/10.1016/j.materresbull.2014.04.072
0025-5408/© 2014 Published by Elsevier Ltd.

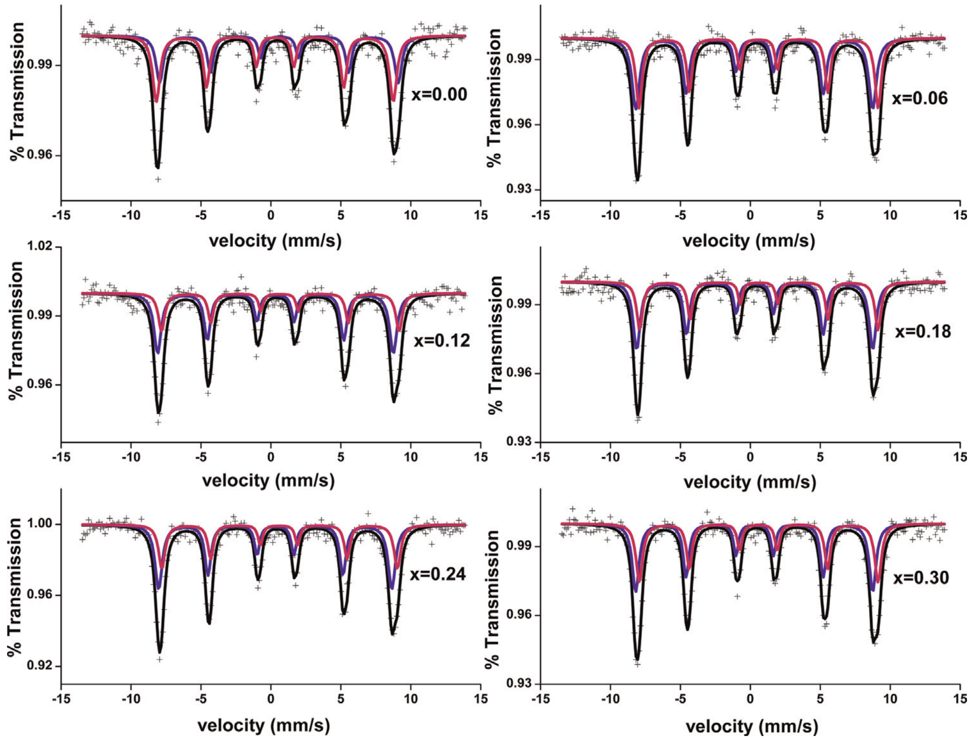

Fig. 1. 5 K Mössbauer spectra of $Ni_{1-x}Cu_xZn_{0.35}Fe_2O_4$ annealed at 1030 °C.

quadruple splitting (Δ), hyperfine field at the nucleus (H_n) and relative proportions of iron for these sextets are given. Velocity calibration has been done by using Mössbauer spectrum of standard natural iron foil while the values of isomer shift are quoted to that of metallic Fe at 300 K.

3. Results and discussion

The Mössbauer spectra of $Ni_{1-x}Cu_xZn_{0.35}Fe_2O_4$ recorded at 5 K which results a typical magnetic structure of ferrite powder as depicted in Fig. 1. The two distinct sextets lying in the resultant spectrum can be attributed to two different environments for Fe ions corresponding to tetrahedral (A) and octahedral (B) sites in the spinel lattice.

An important step in the analysis of the spectra is the identification of sextets corresponding to octahedral and tetrahedral iron ions of the ferrite lattice. It is well known that each A-site ion has 12 B-site neighbors in its immediate surroundings and each B-site ion has 6 A-site nearest neighbors. Fe^{3+}(A)–O^{2-}–Fe^{3+}(B) exchange interaction between iron ions is known to be the strongest, whereas A–A and B–B interactions between iron ions via oxygen ions are relatively weaker. It follows that A-site iron ions are coupled to a large number of Fe bonds as compared to iron ions at B-sites. One therefore expects a larger hyperfine field at the A-site iron nuclei than that at the iron ions at B-sites. Identification of sextets on the basis of hyperfine field offers difficulty at times because in some studies [14–16] hyperfine field at A-site iron nuclei has been reported to be larger than that at B-site iron nuclei and in some other studies [17–20] hyper-fine field at B-site iron nuclei has been reported to be larger than that at A-site iron nuclei.

Hence, in the present study, assignment of sextets corresponding to A- and B-sites has been done on the basis of isomer shift. Since the bond separation between Fe^{3+}—O^{2-} is larger for octahedral ions as compared to that for tetrahedral ions, smaller overlapping of the orbitals of Fe^{3+} ions and oxygen anions and the smaller covalency lead to larger isomer shift at the octahedral site. So the sextet with lower isomer shift corresponds to A-site and the sextet having higher isomer shift represents B-site. In general, the isomer shift at the tetrahedral site is smaller than that at the octahedral site by about 30% [21]. Table 1 gives the hyperfine parameters: isomer shift δ with respect to Co^{57}: Rh, linewidth Γ, quadruple shift Δ, hyperfine field at the nucleus H_n, and relative proportions of iron species assumed to be proportional to the absorption spectral area.

Isomer shift values of all the samples indicate mixed valence states (3^+ and 2^+) for iron. The observed variations in the isomer

Table 1
5 K Mössbauer parameters of $Ni_{1-x}Cu_xZn_{0.35}Fe_2O_4$ annealed at 1030 °C.

Composition	δ (mm/s) ±0.02		Δ (mm/s) ±0.02		H_n (kOe) ±5		Γ (mm/s) ±0.02		(%) Fe ±2	
	B	A	B	A	B	A	B	A	B	A
$Ni_{0.65}Zn_{0.35}Fe_2O_4$	0.59	0.29	−0.05	−0.03	52.91	52.53	0.45	0.446	70.25	29.75
$Ni_{0.59}Cu_{0.06}Zn_{0.35}Fe_2O_4$	0.59	0.29	0.001	−0.04	53.01	52.52	0.47	0.395	69.20	30.20
$Ni_{0.53}Cu_{0.12}Zn_{0.35}Fe_2O_4$	0.64	0.33	0.05	−0.01	52.67	52.27	0.45	0.39	72.20	27.80
$Ni_{0.47}Cu_{0.18}Zn_{0.35}Fe_2O_4$	0.61	0.32	0.01	−0.01	52.85	52.33	0.44	0.37	71.50	28.50
$Ni_{0.41}Cu_{0.24}Zn_{0.35}Fe_2O_4$	0.59	0.32	0.05	−0.02	52.23	51.7	0.45	0.41	72.97	27.03
$Ni_{0.35}Cu_{0.30}Zn_{0.35}Fe_2O_4$	0.59	0.29	0.02	−0.04	52.93	52.56	0.421	0.412	74.6	25.40

Download English Version:

https://daneshyari.com/en/article/1487992

Download Persian Version:

https://daneshyari.com/article/1487992

Daneshyari.com