

Mössbauer studies of Sn⁴⁺/Nb⁵⁺ substituted Mn–Zn ferrites

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Abstract. At room temperature, Mössbauer spectra of Sn⁴⁺/Nb⁵⁺ substituted Mn–Zn ferrites have been taken to understand the site occupancy of substituted ions. The results indicate that both the substituted ions occupy tetrahedral (A) site only at lower concentration of substitution while at higher concentration they occupy both tetrahedral and octahedral sites. At higher concentration of Nb substitution a doublet has been observed besides sextets. The possibility of canting existence on octahedral sites has been discussed. The observed variations of the hyperfine fields, isomer shift, line widths and B/A peak area ratio with the ferrite composition are interpreted.

Keywords. Mn–Zn ferrites; Mössbauer studies.

1. Introduction

The knowledge of cation distribution is important to understand and interpret the physical properties of a ferrite. Mössbauer spectroscopy is a powerful technique to understand the cation distribution over tetrahedral (A) and octahedral (B) sites of spinel structure materials. With the emergence of compact and switched mode power supplies, Mn–Zn ferrite is being used as a core material. The revolutionized technology in the field of communications, devices like computers, microprocessor and VCR systems, the use of above said types of power supplies highly increased. Though studies on Mn–Zn ferrites with the substitution of Sn and Nb were carried out earlier (Inaba *et al* 1994; Rao *et al* 1999), but investigations of Mössbauer spectroscopy were not carried out. Hence, the aim of the present paper is to bring out the Mössbauer studies of Sn/Nb substituted Mn–Zn ferrites.

2. Sample preparation and experimental

Ferrites with the composition, Zn_{0.37-x/2}Mn_{0.58-x/2}M_xFe_{2.05}O₄ (M = Sn⁴⁺/Nb⁵⁺, x = 0.00, 0.15, 0.35 and 0.45), were prepared and the details are given elsewhere (Rao *et al* 1999) along with their characterization. X-ray diffraction pattern confirmed the single-phase formation of ferrite compound. However, at higher concentration of tin substitution the additional phase formation was observed due to the presence of unreacted SnO₂ (Varshney and Puri 1989). For unsubstituted Mn–Zn ferrite the value of lattice parameter (*a*) obtained (8.490 Å) is in agreement with the reported value (8.495 Å) (Rao *et al* 1982). The

room temperature spectra were recorded using a Wissel spectrometer in constant acceleration mode coupled to a 512 MCA Canberra series 35. The radioactive source used in the present study was Co⁵⁷ in a rhodium matrix. Calibration of the spectrometer was done using a standard natural iron foil.

3. Results and discussion

Figure 1 shows the typical Mössbauer spectra of unsubstituted ferrite as well as 0.35 concentration of substitution for both the dopants. The Mössbauer spectra have two sextets corresponding to A and B sites, quadrupole splitting is very small enough to be ignored. Nevertheless, for x ≥ 0.35 of Nb substitution a doublet has been observed besides these two sextets. The spectral lines seem to be quite broad, particularly for site A and spectra seem to appear with relaxation. This is attributed to relaxation phenomena and presence of Fe²⁺ ions at significant concentration. Observed broadening might be due to the combination of unresolved sextets corresponding to A₁ and A₂ or B₁ and B₂. Low temperature study of Mössbauer spectroscopy gives reliable information regarding whether A and or B sites are combination of two sextets or not which gives evidence for the favour of Yafet-Kittel theory (Yafet and Kittel 1952). Earlier studies (Rao 1981) of the present undoped ferrite confirmed the existence of canting. For the present ferrites, from the experimentally observed *M_s* values, the magnetic moment, *n_B(x)* values were evaluated and reported elsewhere (Rao *et al* 1999). Adopting two sublattice models of Neel's (1950) the magnetic moment per formula unit, *n_B(x)^N*, with the known cation distribution at A and B sites are given as

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$$N_B(x)^N = M_B(x) - M_A(x),$$

where M_B and M_A are the magnetic moments of B and A sublattice, $n_B(x)^N$ is the calculated magnetic moment value using Neel's model and x is dopant concentration. The $n_B(x)$ values are obtained at 300 K and these cannot be compared with the $n_B(x)^N$ values which are valid at 0 K. However, the ratio of magnetic moments i.e. $n_B(x)/n_B(0)$, can be compared with $n_B(x)^N/n_B(0)^N$ and a disagreement is found between them. This indicates that significant canting exists on B sites leading to the non-collinear type of magnetic structure.

From the position of the lines of each sextet Mössbauer parameters are derived and these values are given in tables 1–4. For the undoped ferrite, hyperfine field (H_{hff}) reported earlier of the A site Fe nuclei and the B site Fe nuclei were 365.02 and 552.91 KOe, respectively (Rao 1981) (B site sextet was resolved as two components corresponding to B_1 and B_2 sublattices). In the present studies, the H_{hff} values (363.05 and 549.30 KOe) of undoped ferrite are in agreement with the reported (Rao et al 1982) values. At $x = 0.35$ and 0.45 of Nb, a doublet was observed besides sextets. The H_{hff} values of A sites are found to increase in the range 363.05 to 409.31 and 511.08 KOe for Sn and Nb doped ferrites, respectively while B site values decreased initially and then increased and remained almost constant for both the dopants at $x = 0.35$ and 0.45. The variation of Mössbauer parameters depends on the redistribution of Fe ions over A and B sites due to nature and amount of dopant effect. At low concentrations, Sn is known (Rao et al 1999) to occupy tetrahedral (A) sites. As tin (Sn) is doped at the expense of Mn and Zn ions that occupy A site, Sn is expected to occupy A site at low concentrations. Fe content at B sites remains the same. It follows that A site magnetic ions are connected to large number of Fe bonds at B sites rather than B site ions connection to A site magnetic ions resulting in increase and decrease of H_{hff} values of A and B sites, respectively. At higher values of x , dopants occupy B sites (Rao 1981) leading to change of Fe content at B sites, but the increase of B site H_{hff} values can be understood in terms of oxidation (ferrites sintered in air atmosphere) of Fe^{2+} ions by Sn^{4+} ions. The substitution of Nb^{5+} can influence in the same lines besides doublet presence at $x = 0.35$ and 0.45 concentrations due to paramagnetic contribution (Jaji et al 1998).

The increase of isomer shift (IS) values are ascribed to the decrease in s -electron charge distribution of the iron at A and B sites. The difference in the IS values of A and B sites Fe ions is due to sp^3 covalence experienced by the tetrahedral ions. The isomer shift values indicate the valence state of iron as 3+. Line width (LW) values are found to decrease for tetrahedral (A) sites. However, for B sites, the same is (LW values) found to decrease compared to undoped ferrite. Nevertheless no significant change is found with dopant concentration (x). The

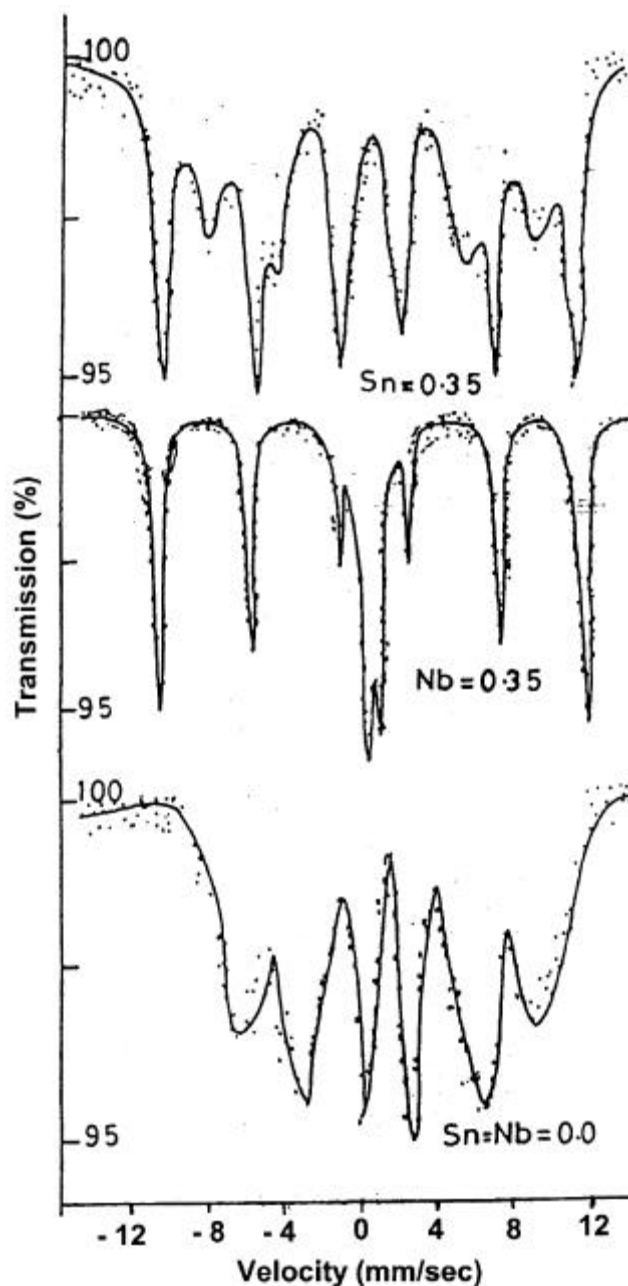


Figure 1. Mössbauer spectra of ferrites at $x = 0.00$ and 0.35 conc. of substituted ions.

Table 1. Hyperfine fields variation with dopant concentration (error ± 5.0).

Dopant conc.	Hyperfine field (KOe)			
	Tin		Niobium	
	Sextet A	Sextet B	Sextet A	Sextet B
0.00	363.05	549.30	365.05	549.30
0.15	379.60	451.20	471.30	539.20
0.35	393.90	492.70	504.30	514.20
0.45	409.31	490.83	511.08	512.49

Table 2. Isomer shift variation with dopant concentration (error ± 0.04).

Dopant conc.	Isomer shift (mm/s)			
	Tin		Niobium	
	Sextet A	Sextet B	Sextet A	Sextet B
Tin/niobium				
0.00	0.181	0.348	0.181	0.348
0.15	0.307	0.432	0.341	0.357
0.35	0.381	0.453	0.367	0.369
0.45	0.366	0.507	0.374	0.377

Table 3. Line width variation with dopant concentration (error ± 0.01).

Dopant conc.	Line width (mm/s)			
	Tin		Niobium	
	Sextet A	Sextet B	Sextet A	Sextet B
Tin/niobium				
0.00	1.48	1.96	1.48	1.96
0.15	0.896	1.611	0.378	0.399
0.35	0.655	1.603	0.366	0.321
0.45	0.661	1.600	0.358	0.306

Table 4. (B/A) peak area ratio variation with dopant concentration and doublet values of niobium at 0.35 and 0.45.

Dopant conc.	(B/A) peak ratio		Doublet		
			X = 0.35	X = 0.45	
	Tin	Niobium	Niobium		
0.00	2.146	2.146	Q.S	0.479	0.486
0.15	1.589	1.427	I.S	0.365	0.372
0.35	1.469	1.211	L.W	0.468	0.481
0.45	1.347	1.126	Area	0.336	0.357

observed peak area ratio (B/A) of A and B sites decreases with x . The occupation of non-magnetic ions at B sites

change their area. Finally we can conclude that these dopants initially ($x = 0.15$) occupy tetrahedral (A) sites and for higher concentration ($x = 0.35$ and 0.45) occupy octahedral (B) sites displacing B site Fe^{3+} ions to A sites. The possible cation distribution is $(\text{Zn}_{0.37-x/2}\text{Mn}_{0.58-x/2}\text{M}_{x-k}\text{Fe}_{0.05+k}^{3+})[\text{Fe}_{1.95-k}^{3+}\text{M}_k\text{Fe}_{0.05}^{2+}]\text{O}_4^{-2}$, k appears only when $x \neq 0$, otherwise k will be zero for $x = 0$.

4. Conclusions

- (I) In Mössbauer spectra sextets corresponding to A and B sites are observed and at higher concentration of Nb quadrupole splitting are observed besides sextets.
- (II) Spectral lines seem to be broad.
- (III) The magnetic field values are found to increase at tetrahedral sites while at octahedral sites these initially decrease, then increase and remain constant.
- (IV) Isomer shift values indicate that the valence state of iron as $3+$.
- (V) From the results it is concluded that both the dopant initially occupy A site and later occupy both A and B sites.

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