

Infrared absorption spectroscopic study of Nd³⁺ substituted Zn–Mg ferrites

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MS received 13 November 2001; revised 20 May 2002

Abstract. Compositions of polycrystalline Zn_xMg_{1-x}Fe_{2-y}Nd_yO₄ ($x = 0.00, 0.20, 0.40, 0.60, 0.80$ and 1.00 ; $y = 0.00, 0.05$ and 0.10) ferrites were prepared by standard ceramic method and characterized by X-ray diffraction, scanning electron microscopy and infrared absorption spectroscopy. Far infrared absorption spectra show two significant absorption bands, first at about 600 cm⁻¹ and second at about 425 cm⁻¹, which were respectively attributed to tetrahedral (A) and octahedral (B) sites of the spinel. The positions of bands are found to be composition dependent. The force constants, K_T and K_O , were calculated and plotted against zinc concentration. Compositional dependence of force constants is explained on the basis of cation–oxygen bond distances of respective sites and cation distribution.

Keywords. Polycrystalline ferrites; rare earth; IR absorption; cation distribution; force constants.

1. Introduction

Infrared absorption spectroscopy is an important and non-destructive characterizing tool, which provides qualitative information regarding structural details of crystalline materials (Ishil *et al* 1972; Murthy *et al* 1978). The results from IR absorption study can be used to interpret the electrical and magnetic properties of the ferrites (Braber 1969). The absorption bands, from which the details regarding functional groups and their linkages can be explored, are found to be dependent on atomic mass, cationic radius, cation–anion bond distances, cation distribution etc. Infrared spectral analyses have been carried out for several ferrites by Woldron (1955) who reported two absorption bands within the wave numbers 800–200 cm⁻¹, which could be respectively attributed to the tetrahedral and octahedral group complexes of the spinel structure. El Hitti *et al* (1996) studied the IR absorption spectra of Ni–Zn–Mg ferrites and reported four absorption bands, out of which n_1 and n_2 are due to tetrahedral and octahedral sites and n_3 and n_4 are assigned to the vibrations in divalent metal ion–oxygen group complexes in octahedral site (Josyulu and Sobhanadri 1981) and mass of divalent cations (Preudhomme and Tarte 1971), respectively. Kolekar *et al* (1994) studied the Gd³⁺ substituted Cd–Cu ferrite system by using IR absorption spectroscopy and the results showing the compositional dependent behaviour of force constant are attributed to the cation oxygen bond distances. The structural distortion

in case of chromium substituted nickel ferrites was studied by Ghatage *et al* (1996) and the existence of fine structure is attributed to the Jahn-Teller effect. The IR spectra of Cd, Co, Mg, Ni, Zn, Cu etc containing ferrites have been reported (Srivastav and Srinivasan 1982; Nathwani and Darshane 1987). But the reports on rare-earth substituted Zn–Mg ferrites are rather rare. In the present communication the results regarding IR absorption spectral analysis of Nd³⁺ substituted Zn–Mg ferrites are discussed.

2. Experimental

Compositions of Zn_xMg_{1-x}Fe_{2-y}Nd_yO₄ ($x = 0.00, 0.20, 0.40, 0.60, 0.80$ and 1.00 ; $y = 0.00, 0.05$ and 0.10) ferrites were prepared by using standard ceramic method, wherein the oxides ZnO, MgO, Fe₂O₃ and Nd₂O₃ of AR grade were used in stoichiometric weight proportion. The sintering temperature was controlled at 1000°C for 24 h and then slowly cooled, at the rate of 80°C/h, to room temperature. To confirm the completion of solid state reaction the compositions were subjected to characterization by X-ray diffraction, scanning electron microscopy and infrared absorption spectroscopy. The IR absorption spectra of finely crushed powder of the compositions were obtained, in the range from 800 cm⁻¹ to 200 cm⁻¹, by using Perkin-Elmer Spectrophotometer model 783, wherein KBr is used as solvent in 1 : 3 proportion. The spectrum, transmittance (%) against wavenumber (cm⁻¹), is used for interpretation of the results.

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3. Results and discussion

X-ray diffractograms of powdered compositions under investigation reveal the formation of single phase cubic spinels, showing well defined reflection of allowed planes. The results regarding X-ray analysis are reported elsewhere (Ladgaonkar *et al* 2000a).

Far infrared absorption spectra for all compositions are obtained from IR spectrometer and the typical spectra for the compositions $x = 0.20$; $y = 0.00, 0.05$ and 0.10 are depicted in figure 1. On inspection of figure, it is found that the spectra consist of two significant absorption bands, first at about 600 cm^{-1} and second at about

425 cm^{-1} . Absorption bands observed within this limit reveal the formation of single phase spinel structure having two sublattices, tetrahedral (A) site and octahedral (B) site (Woldron 1955). The absorption band, \mathbf{n}_1 , observed at about 600 cm^{-1} is attributed to the tetrahedral site, whereas that of \mathbf{n}_2 observed at about 425 cm^{-1} is assigned to octahedral group complexes. The positions of absorption bands, in wave numbers, are presented in table 1. From this table, it is found that the positions of bands are composition dependent and show close agreement with the previous reports (Josyulu and Sobhanadri 1981; El Hitti *et al* 1996). The wave number of band, \mathbf{n}_1 , shows a decrease with increasing zinc concentration (x). This

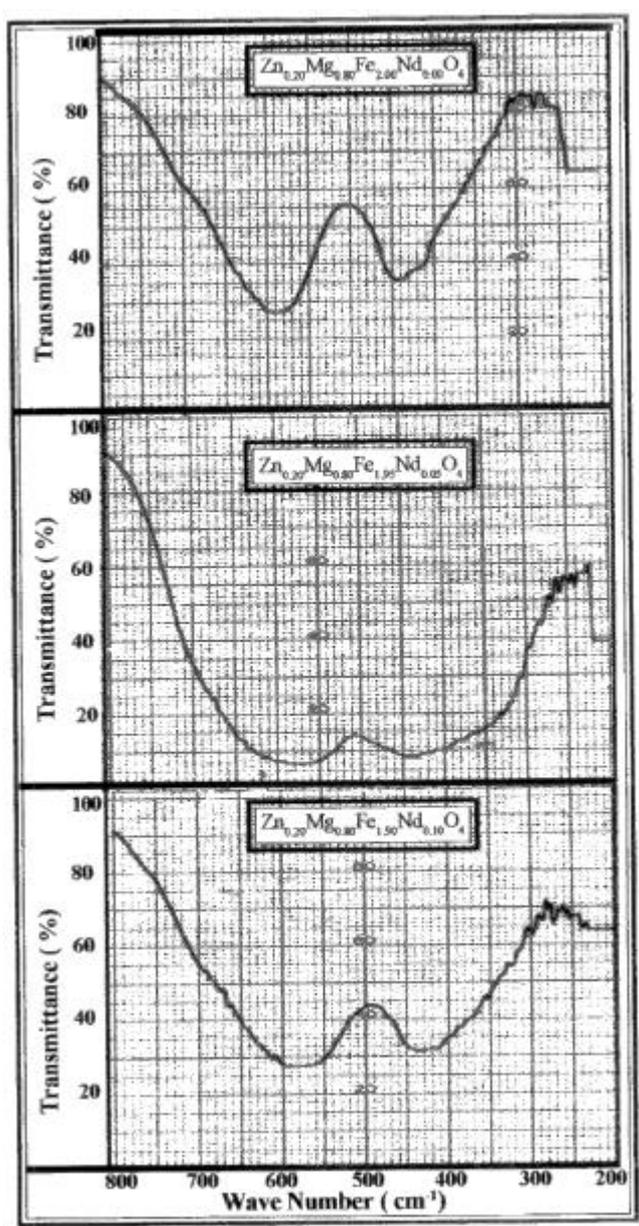


Figure 1. Infrared absorption spectra for compositions $\text{Zn}_{0.20}\text{Mg}_{0.80}\text{Fe}_{2-y}\text{Nd}_y\text{O}_4$ for $y = 0.00, 0.05$ and 0.10 .

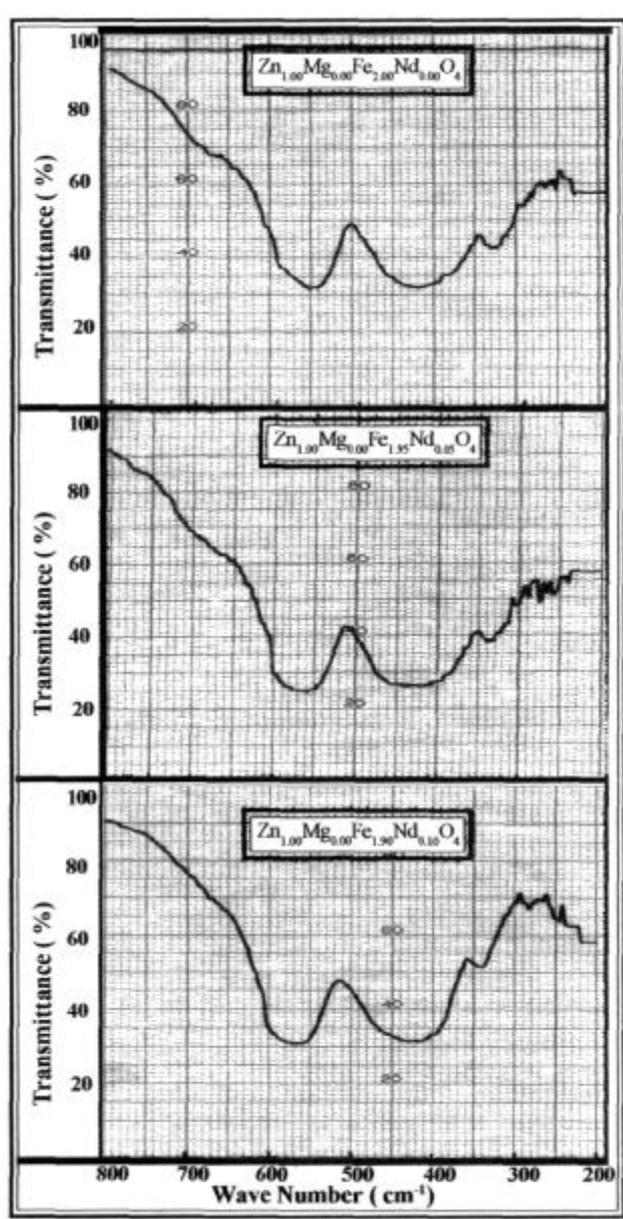


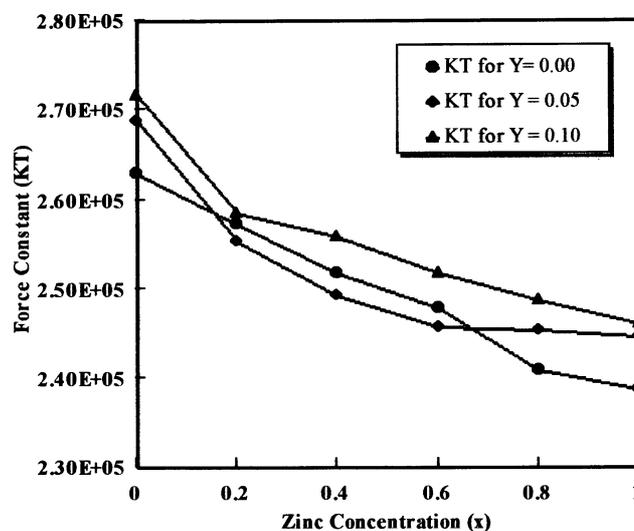
Figure 2. Infrared absorption spectra for compositions $\text{Zn}_{1.00}\text{Mg}_{0.00}\text{Fe}_{2-y}\text{Nd}_y\text{O}_4$ for $y = 0.00, 0.05$ and 0.10 .

Table 1. Infrared absorption bands, cation oxygen bond distances and cation distribution for compositions $Zn_xMg_{1-x}Fe_{2-y}Nd_yO_4$ ferrite system.

Conc. $Zn^{2+}(x)$	Conc. $Nd^{3+}(y)$	Wave number of absorption bands (n) cm^{-1}			Cation distribution	Cation–oxygen bond distance (Å) for tetrahedral (A) and octahedral (B) sites	
		n_1	n_2	n_3		(A–O)	(B–O)
0.00		585	430	–	$(Zn_{0.00}Mg_{0.124}Fe_{0.876})^A[Mg_{0.876}Fe_{1.124}Nd_{0.00}]^BO_4$	1.718	2.133
0.20		585	445	–	$(Zn_{0.20}Mg_{0.186}Fe_{0.614})^A[Mg_{0.614}Fe_{1.386}Nd_{0.00}]^BO_4$	1.780	2.105
0.40	0.00	580	440	–	$(Zn_{0.40}Mg_{0.176}Fe_{0.424})^A[Mg_{0.424}Fe_{1.576}Nd_{0.00}]^BO_4$	1.820	2.089
0.60		570	440	–	$(Zn_{0.60}Mg_{0.063}Fe_{0.337})^A[Mg_{0.337}Fe_{1.663}Nd_{0.00}]^BO_4$	1.855	2.077
0.80		560	435	–	$(Zn_{0.80}Mg_{0.009}Fe_{0.191})^A[Mg_{0.191}Fe_{1.809}Nd_{0.00}]^BO_4$	1.871	2.075
1.00		555	430	330	$(Zn_{1.00}Mg_{0.000}Fe_{0.000})^A[Mg_{0.000}Fe_{2.000}Nd_{0.00}]^BO_4$	1.943	2.041
0.00		600	440	–	$(Zn_{0.00}Mg_{0.125}Fe_{0.875})^A[Mg_{0.875}Fe_{1.075}Nd_{0.05}]^BO_4$	1.706	2.132
0.20		580	440	–	$(Zn_{0.20}Mg_{0.198}Fe_{0.602})^A[Mg_{0.602}Fe_{1.348}Nd_{0.05}]^BO_4$	1.776	2.101
0.40	0.05	570	430	–	$(Zn_{0.40}Mg_{0.193}Fe_{0.407})^A[Mg_{0.407}Fe_{1.543}Nd_{0.05}]^BO_4$	1.813	2.086
0.60		565	430	–	$(Zn_{0.60}Mg_{0.086}Fe_{0.314})^A[Mg_{0.314}Fe_{1.636}Nd_{0.05}]^BO_4$	1.850	2.073
0.80		563	435	–	$(Zn_{0.80}Mg_{0.024}Fe_{0.176})^A[Mg_{0.176}Fe_{1.774}Nd_{0.05}]^BO_4$	1.869	2.069
1.00		560	430	335	$(Zn_{1.00}Mg_{0.000}Fe_{0.000})^A[Mg_{0.000}Fe_{1.950}Nd_{0.05}]^BO_4$	1.924	2.045
0.00		600	440	–	$(Zn_{0.00}Mg_{0.128}Fe_{0.872})^A[Mg_{0.872}Fe_{1.028}Nd_{0.10}]^BO_4$	1.695	2.131
0.20		580	435	–	$(Zn_{0.20}Mg_{0.208}Fe_{0.592})^A[Mg_{0.592}Fe_{1.308}Nd_{0.10}]^BO_4$	1.757	2.103
0.40	0.10	575	430	–	$(Zn_{0.40}Mg_{0.202}Fe_{0.398})^A[Mg_{0.398}Fe_{1.502}Nd_{0.10}]^BO_4$	1.776	2.100
0.60		570	430	–	$(Zn_{0.60}Mg_{0.084}Fe_{0.316})^A[Mg_{0.316}Fe_{1.584}Nd_{0.10}]^BO_4$	1.795	2.097
0.80		565	430	–	$(Zn_{0.80}Mg_{0.020}Fe_{0.180})^A[Mg_{0.180}Fe_{1.720}Nd_{0.10}]^BO_4$	1.828	2.085
1.00		560	425	340	$(Zn_{1.00}Mg_{0.000}Fe_{0.000})^A[Mg_{0.000}Fe_{1.900}Nd_{0.10}]^BO_4$	1.904	2.047

variation in the band positions may be due to variations in the cation–oxygen bond (A–O) lengths (Kolekar *et al* 1994). Zinc ion, which when substituted, resides on tetrahedral (A) site, displacing proportional amount of Fe^{3+} ion from A to B site. This leads to increase in the cation–oxygen bond length of tetrahedral lattice site (A) of the spinel (Ladgaonkar *et al* 2000b), which results into decrease in the wave number of n_1 band. For $MgFe_2O_4$, two bands, n_1 and n_2 , have been observed (Woldron 1955). However, in case of $x = 1$, i.e. for zinc rich compositions, as indicated in figure 2, the third band (n_3) of very low intensity closer to n_2 is observed. Many researchers (Liene 1973; Josyulu and Sobhanadri 1981; El Hitti *et al* 1996) have also reported this third band in case of zinc rich compositions, assigning it to the divalent octahedral metal ion–oxygen group complexes.

On substitution of Nd^{3+} ion the position of n_2 band shifts towards lower side, which suggests the occupancy of Nd^{3+} ion on octahedral (B) site. The results regarding d.c. electrical resistivity study support the B-site occupancy of neodymium showing increase in the d.c. resistivity due to its impediment to the electrical conduction (Ladgaonkar *et al* 2001). The magnetization study also supports the occupancy of neodymium ion on B-site showing dilution in the magnetization (Ladgaonkar *et al* 2000a). However, on Nd^{3+} ion substitution, the broadening of n_2 band takes place (figure 1), which may be due to occupancy of cations of different characters on the same site (Kolekar *et al* 1994).

**Figure 3.** Graph of force constant, K_T , against zinc conc. (x) for $y = 0.00, 0.05$ and 0.10 .

The force constants, for tetrahedral site (K_T) and octahedral site (K_O), were calculated employing the method suggested by Woldron (1955). According to Woldron, the force constants, K_T and K_O , for respective sites are given by,

$$K_T = 0.0446 \times n_1^2 \times M_2 \times [V/(V + 3)], \quad (1)$$

$$K_O = (0.94218) \times [M_1/n_1^2], \quad (2)$$

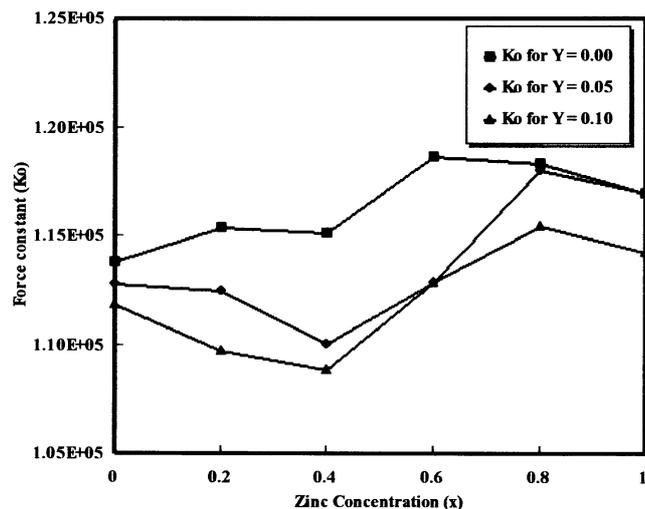


Figure 4. Graph of force constant, K_O , against zinc conc. (x) for $y = 0.00, 0.05$ and 0.10 .

where,

$$V = (64 - [2M_1 \times U])/M_2, \quad (3)$$

and

$$U = 2K_O/(2M_1 - 2K_O), \quad (4)$$

where, M_1 and M_2 are the molecular weights of cations on A and B sites, respectively. The cation distribution required for estimation of the force constants is obtained from theoretical X-ray intensity calculation method (Ladgaonkar and Vaingankar 1998; Ladgaonkar 2000) and is published elsewhere (Ladgaonkar *et al* 2001). The results are presented in table 1.

The values of force constants were calculated by using (1) and (2), as a function of zinc concentration. To study the compositional dependence, the force constants, K_T and K_O , are plotted against zinc concentration (x) and presented in figures 3 and 4, respectively. On inspection of figure 3, it is observed that the force constants of tetrahedral site (K_T) decreases with increasing zinc concentration. This behaviour can be attributed to the variation in cation oxygen bond lengths, which are estimated from X-ray analysis and included in table 1. Bond lengths, A–O, increase with increasing zinc concentration. The energy required to break longer bonds is less. This supports decrease in the force constant of tetrahedral site, supporting predicted cation distribution, wherein zinc strongly occupies A site and magnesium ion gets preferentially distributed among A and B sites. However,

on neodymium substitution the octahedral force constant (K_O) is found to decrease (figure 4), which supports the occupancy of neodymium on B site.

4. Conclusions

Infrared absorption spectra of the compositions under investigation reveal formation of single phase cubic spinel, showing two significant absorption bands. The positions of absorption bands are compositional dependent, whose dependence could be attributed to the variation in cation oxygen bond distances. Variations in the force constants of tetrahedral and octahedral sites support predicted cation distribution, wherein zinc shows strong occupancy to A site and magnesium and iron ions distribute preferentially among A and B sites. Neodymium occupies octahedral site.

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