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Structural, optical and electrical properties of chemically derived nickel substituted zinc ferrite nanocrystals

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HIGHLIGHTS

- Pure single phase nanocrystalline Zn/Ni ferrites by facile soft chemical route.
- Changes in microstructural parameters of Zn ferrite is observed due to Ni inclusion.
- Optical band gap shows a maximum while the concentration of Ni increases.
- Inverse to spinal ferrite change is observed in ac and dc electrical properties.

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ABSTRACT

Single phase spinel Ni substituted nanocrystalline Zn ferrites have been synthesized using a soft chemical route. Effect of Ni substitution on structure, electrical and optical properties has been investigated. X-ray diffraction study confirms the growth of single phase nanocrystalline Ni substituted Zn ferrites. FTIR and UV–Visible studies delineate the change in structure and optical band gap due to inclusion of Ni ions. Substitution of Ni ion has been manifested on lattice parameter which systematically decreases from 8.448 Å to 8.280 Å. An initial increase followed by subsequent decrease in optical band gap with the increase in Ni content is observed. In addition, both ac and dc electrical studies shows anomalous behavior in conductivity and dielectric properties for the samples having Ni content in the range 0.2–0.6 mol fraction which can be attributed to the normal to inverse spinel structural changes.

1. Introduction

The nanocrystalline ferrite has been subject of intensive research and become important from both the fundamental as well as application point of view as they got potential use in multilayer chip inductor (MLCI), ferrofluids, high-speed digital tape or recording disks, rod antenna, humidity sensor etc. [1,2]. Ferrite nanocrystals are also promising candidates for various applications, such as inter-body drug delivery [3], bio separation, and magnetic refrigeration systems [4], in particular due to their specific property namely, superparamagnetism. In addition, among ferrospinels zinc ferrites are used in gas sensing, catalytic application [5,6], etc. These materials are also very good dielectric materials and have many applications in technology ranging from microwave to radio frequency. It can be used as microwave absorbers. Some ferrites absorb microwave by losing interaction of the electric and magnetic field vector of incident wave and in the process transfer microwave energy into thermal energy. Radar absorbing paint made from ferrite can be used to coat military aircraft for stealth operation.

Spinel ferrites have common formula $(A^{2+})[B^{3+}]_2O_4$. The unit cell of the spinel structure involves 64 tetrahedral (A) sites and 32 octahedral [B] sites among which 8 tetrahedral and 16 octahedral sites are occupied by divalent or trivalent ions. Distribution of divalent and trivalent cations between the tetrahedral and octahedral sites in spinel ferrites can be expressed with formula $(A^{2+}{}_{\delta}\ B^{3+}{}_{1-\delta})[A^{2+}{}_{1-\delta}\ B^{3+}{}_{1+\delta}]O_4$, where δ is the degree of inversion. For normal ferrite δ is 1 whereas δ is 0 for inverse spinel structure. In a mixed spinel structure with δ between 1 and 0 both the tetrahedral and octahedral sublattice sites are occupied by divalent and trivalent ions.

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Ni–Zn ferrites have been used for many years in the electrical and electronics industries. It is a soft magnetic ceramic having cubic spinel configurations which has a unit cell consisting of eight formula unit of the type $(Zn_xFe_{1-x})_A[Ni_{1-x}Fe_{1+x}]_BO_4$ where 'A' represents tetrahedral site and 'B' the octahedral site [7,8]. Several novel methods of synthesis of nanocrystalline ferrites such as sol–gel [9,10] co-precipitation [11,12], oxidation [13] and reverse micelle technique [14,15] have been explored previously. The properties of ferrites are very much sensitive to methodology adopted for their synthesis, preparative parameters, initial ingredients, etc. [16,17].

In our previous work, with the same system [18], we have successfully investigated the structural changes that took place with the variation of Ni percentage by positron annihilation technique. In this work, we have tried to investigate whether the same phenomenon is reflected in the same composition region, by their optical and electrical studies.

2. Experimental

The Ni substituted zinc nanoferrites $Ni_xZn_{1-x}Fe_2O_4$ ($x = 0.0, 0.2, 0.4, 0.6, 0.8, 1.0$) were prepared by mixing aqueous solutions of calculated amounts of zinc nitrate ($Zn(NO_3)_3{\cdot}9H_2O$), ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) and nickel nitrate ($Ni(NO_3)_2{\cdot}6H_2O$) procured from MERCK. Sodium hydroxide (NaOH) solution was added drop by drop for precipitation to occur. The precipitate was washed several times with water, dried and annealed at 773 K for 30 min.

X-ray diffractograms of the samples were recorded using X Pert Pro X-ray diffractometer (PANLYTICAL, Almelo, The Netherlands) fitted with nickel-filtered Cu K_α radiation ($\lambda = 1.5414$ Å) in 2θ range from 20 to 90^0. Infra-red spectra were recorded by Nicolet Magma-IR (750, Series II) spectrophotometer in the range 400–4000 cm^{-1} using KBr pellet technique. The optical absorption spectra of samples were recorded at room temperature in the range 200–800 nm using a double beam Hitachi spectrophotometer (model U3410).

The electrical measurements were carried out at different temperatures starting from 443 K up to 563 K and in the frequency range 20 Hz to 2 MHz, using Agilent high precession LCR meter (Model E4980A). For electrical study prepared powders were pressed into pellet form which was painted on either side with silver paste to ensure good electric contacts. A.C. electrical conductivity as well as the dielectric parameters such as dielectric constant and loss tangent were measured and analyzed.

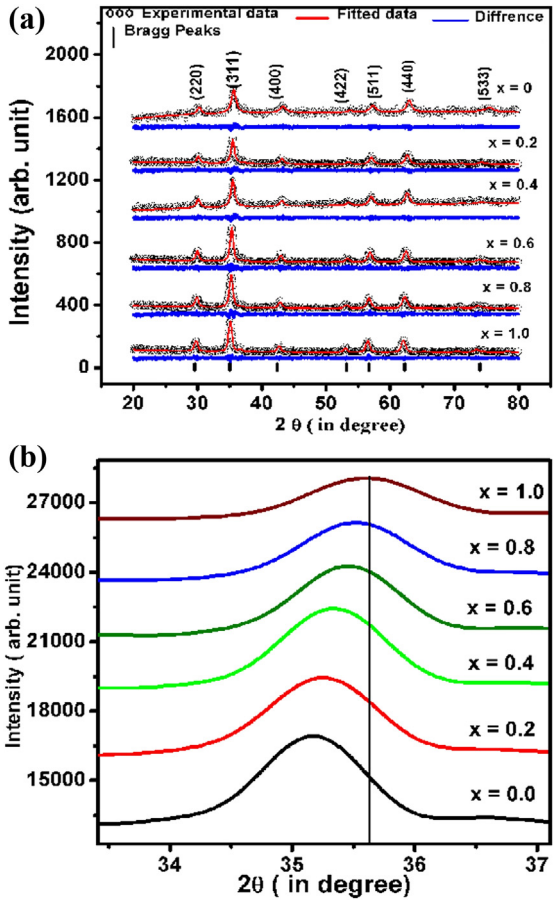

Fig. 1. (a): X-ray diffraction patterns of $Ni_xZn_{1-x}Fe_2O_4$ (x = 1, 0.8, 0.6, 0.4, 0.2, 0) (b): Shifting of strongest peak due to Ni inclusion.

3. Results and discussions

3.1. X-ray analysis and Rietveld refinement

The X-Ray diffraction patterns with Rietveld refinement fitting of all the prepared samples are shown in Fig. 1(a). It is observed that all the peaks are matched well with the standard data (JCPDS Card no. #221012 and #441485) which indicates the growth of pure single phase ferrites. The systematic shift of the peak towards larger 2θ (Fig. 1(b)) with increasing Ni content indicates lattice contraction.

The crystallite diameters d_c were estimated from the X-ray diffraction data using the Debye-Scherrer equation.

$$d_c = \frac{0.89\lambda}{\beta\cos\theta} \quad (1)$$

where β in eq. (1) refers to the full width at half maximum of the concerned peak. The two most intense reflections i.e. (311) and (440) for each sample have been considered here to estimate the average crystallite size. The lattice parameter α was obtained using the relation between separation d_{lmn} of the planes and the Miller indices (lmn) given by,

$$d_{lmn} = \frac{\alpha}{\sqrt{l^2 + m^2 + n^2}} \quad (2)$$

and from Rietveld refinement. It has been observed that the lattice parameter showed a continuous decreasing tendency with the increase in Ni concentration whereas particle size in the samples remain close to each other (Table 1(a) and (b)). The decrease in lattice parameter may be due to the substitution of smaller Ni^{2+} (0.83 Å) ions in place of larger Zn^{2+} ions (0.88 Å) in the system. Since smaller ions are replacing larger ones, decrease in the lattice parameter α is expected.

Detailed structural and microstructural characterization has

Table 1a
Calculated Lattice parameter (α) and the average particle size (d_c) of the samples with different compositions from Debye-Scherrer equation.

Ni concentration (x)	Highest peak position 2θ(deg)	Particle size (nm)	2nd Highest peak position 2θ(deg)	Particle size (nm)	Average particle size (nm)	Lattice parameter (α) in Å
x = 0.0	35.18	14.70	29.74	14.90	14.80	8.448
x = 0.2	35.30	12.57	29.86	13.10	12.75	8.416
x = 0.4	35.46	14.01	29.98	13.99	14.00	8.382
x = 0.6	35.55	14.27	30.26	14.50	14.39	8.348
x = 0.8	35.67	13.36	30.54	13.56	13.46	8.314
x = 1.0	35.86	12.84	30.73	12.96	12.90	8.280