Cation Distribution And Infrared Studies On In^{3+} Substituted Nanocrystalline Ferrite

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Abstract

Nanocrystalline spinel ferrite with composition $Mn_{0.8}Zn_{0.2}In_{0.100}Fe_{1.900}O_4$ were prepared by oxalate co-precipitation technique followed by microwave heating. Formation of face centered cubic spinel structure was verified by X-ray diffraction. Cation distribution was studied by full profile fitting of X-ray diffraction pattern using GSAS II (General Structure Analysis System). Substantial redistribution of cations is observed at tetrahedral and octahedral sites in naocrystalline ferrites. Two prominent absorption bands are observed in FTIR spectra in the range 350-800 cm^{-1}. These bands represent position of cations in spinel lattice and their vibration modes. Lowering of crystalline symmetry resulted in splitting and emergence of additional absorption bands in FTIR spectra.

Keywords: Ferrites, Co-precipitation, XRD, FTIR, Rietveld refinement, Cation distribution.

1. Introduction

Spinel ferrites are semiconducting oxide materials. They are used in variety of applications, that are based on the chemical and physical properties of ferrites such as high saturation magnetization and electrical resistivity, low electrical losses, and good chemical stability [1].

Spinel ferrites belong to space group Fd3m. Face centered cubic spinel structure contains two types of interstitial sites: 64 tetrahedral sites and 32 octahedral sites in a unit cell containing 8 units of basic formula AB_2O_4. Of all, cations occupy one-eighth of tetrahedral sites and half of octahedral sites. [1]. Cation distribution between the tetrahedral and octahedral sites for spinel ferrites has been a subject of many studies [2, 3] because theoretical interpretation of the chemical and physical properties (magnetic, electrical, catalytic, etc.) of ferrites depends on the sites assigned to the cations. The distribution of cations depends upon various parameters like method of preparation, synthesis temperature and atmosphere, and amount of dopant [4].

The arrangement of metal ions between tetrahedral and octahedral sites is important in tailoring magnetic properties of spinel ferrites. This is so because total magnetic moment appears due to anti-parallel alignment of electron spins between tetrahedral and octahedral sites [5]. The FTIR spectral study is an important tool in the investigation of structural properties of ferrites. The absorption bands in FTIR spectra of spinel ferrites are caused due to lattice vibrations of oxide ions with cations. The frequencies of vibrations are complex interplay of cation masses, the lattice parameters and the type of cation-anion bond, etc [6].

2. Experimental method

Nanocrystalline soft ferrite with composition $Mn_{0.8}Zn_{0.2}In_{0.100}Fe_{1.900}O_4$ was synthesized by oxalate co-precipitation technique and microwave sintering. Manganese sulfate monohydrate ($MnSO_4$ .H_2O 99%, Merck), Iron (II) sulfate heptahydrate ($FeSO_4.7H_2O$ 99%, Merck), Zinc sulfate heptahydrate ($ZnSO_4.7H_2O$ 99%, Merck) were used as starting materials. The details of preparation method are given elsewhere [7]. However in brief, metal sulfates were dissolved in double distilled water at room temperature. The aqueous solution of di-ammonium oxalate monohydrate was rapidly added to the sulfate solutions under continuous stirring. Bright yellow precipitates were allowed to settle in the beaker. Excess ammonium oxalate and sulfate contaminant in the precipitates were washed by using distilled water. The precipitates were dried in an oven at 100° C for 8 hours. The dried precipitates were poured in quartz crucible. Thereafter, crucible was placed in a cylindrical cavity created inside a high alumina. The gap between quartz crucible and wall of the cavity was filled with aluminium powder. The metal oxalates are poor absorbers of

microwave radiation hence it was necessary to use microwave susceptor for heating. The high alumina brick containing susceptor (aluminium powder), crucible with dried precursor was placed on the turn table of commercial microwave oven (ONIDA, 25XL Power convection) operated at frequency 2.45 GHz and maximum output power 900 Watts. The oven was operated at 60% of optimum power for 630 seconds to take the temperature of precursors to 450 °C. Brick was immediately brought out of the oven and allowed to cool.

The X-ray diffraction patterns were recorded in the scattering range (2θ) of 10˚-100˚, scan rate of 0.05˚ per second and a primary beam power of 40kV, 30mA using a Bruker AXS D8 Advance X-ray diffractometer with Cu-Kα radiation (λ=1.54058 Å). The lattice parameters, the oxygen position parameter and cation distribution was determined by Rietveld refinement of X-ray diffraction pattern. General Structure Analysis System (GSAS II) was employed for this purpose [8].

FTIR spectra were recorded in the range 350-800 cm^{-1} on Perkin Elmer spectrum one spectrophotometer by forming pellet of sample dispersed in KBr. FTIR spectra were recorded in order to verify the nature of chemical bonds in the spinel.

3. Results and discussions

Rietveld refinement is an excellent technique for structural determination and refinement from powder diffraction data. This method uses a least square method to compare observed Bragg's intensities and calculated intensities based on possible structural model. Various structural parameters of the model are varied in order to ensure the best possible fit to experimentally observed data.

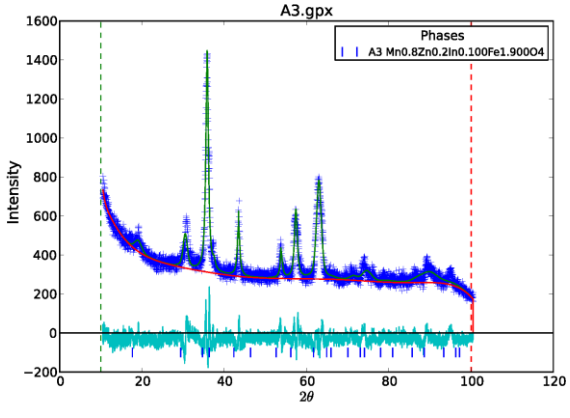

Figure1. Full profile fitting of X-ray diffraction pattern of $Mn_{0.8}Zn_{0.2}In_{0.100}Fe_{1.900}O_4$.

Plots of the Rietveld refinement are given in Figure 1. Observed data is plotted in dark blue + symbol. Calculated patterns are shown in green solid line. The difference curve (observed intensity – calculated intensity) is the lowermost. The Reliability parameters, lattice parameter, oxygen position parameter and cation distribution is shown in Table 1.

Reliability parameters indicate the quality of fit to experimental data. Low values of R_w and Goodness of Fit(GOF) indicates high confidence in simulated values obtained from the fit. In the bulk material the divalent ions such as Fe^{2+},Co^{2+},Cu^{2+} and Mg^{2+} prefer B sites, whereas Zn^{2+} ions occupy A sites [9 , 10 , 5]. At nanoscale Zn ferrite has mixed cation distribution because some percentage of Zn^{2+} ions occupy 16d sites [10, 5]. In bulk Mn ferrites 80% of Mn^{2+} ions occupy tetrahedral sites and remaining are in octahedral sites [9]. Bulk manganese ferrite has mixed cation distribution because Mn^{2+} and Fe^{3+} ions occupy tetrahedral as well as octahedral sites. In tetrahedral site Mn^{2+} is found in +2 and +4 oxidation states [10]. In case of Mn-Zn ferrites, when the nonmagnetic zinc ion is substituted into the manganese ferrite lattice, it has a stronger preference for the tetrahedral site as compared to ferric ion and thus reduces the amount of Fe^{3+} on the A site [11].

In our study, only 22% of Mn^{2+} ions occupy tetrahedral site, whereas 47% of the Zn^{2+} ions are in terahedral site. This is substantial redistribution of cations. This work has been successful in incorporating large fraction of diamagnetic Zn^{2+} ions in octahedral sites in order decrease the magnetic moment of the A-sublattice, this increases the overall magnetization of the crystal.

Table1. Cation distribution and essential parameters as obtained from Rietveld refinement of X- ray diffraction pattern for $Mn_{0.8}Zn_{0.2}In_{0.100}Fe_{1.900}O_4$.

Parameter	**Fitted values**
Lattice parameter	8.43 nm
R- factor (R_w)	7.41%
Goodness of fit (*GOF*)	1.88
Oxygen position parameter (u)	0.262
Octahedral site occupancy	$Mn_{0.621}Zn_{0.106}In_{0.032}Fe_{1.174}$
Tetrahedral site occupancy	$Mn_{0.178}Zn_{0.094}In_{0.068}Fe_{0.726}$

Infrared spectroscopy is used to verify local symmetry, ordering phenomenon, presence or absence of Fe^{2+} ions, force constant and elastic moduli of ferrite systems [12]. Lattice vibrations of oxygen ions against the cations give rise to two prominent absorption bands between 400 to 700 cm^{-1}. These are attributed to tetrahedral and octahedral site complexes in spinel structure [13].

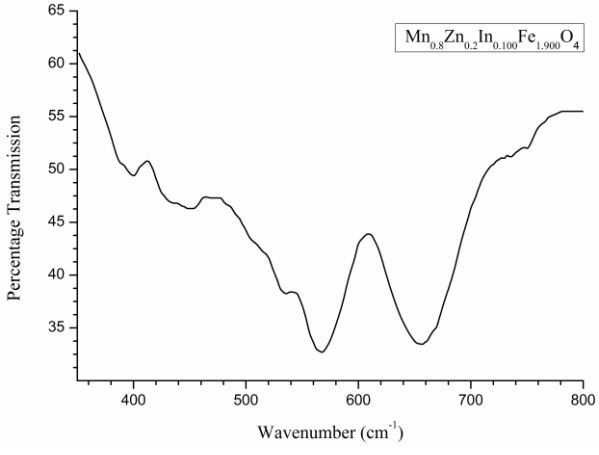

Figure 2. FTIR spectra of $Mn_{0.8}Zn_{0.2}In_{0.100}Fe_{1.900}O_4$.

Table 2. Absorption bands for $Mn_{0.8}Zn_{0.2}In_{0.100}Fe_{1.900}O_4$.

Absorption band	Absorption band position (cm^{-1})
ν_1''	653.4
ν_1'	565.2
ν_2'''	532.3
ν_2''	449.3
ν_2'	400.0

FTIR spectra in Figure 2 represents various absorption bands as tabulated in table 1. The high intensity absorption bands at 653.4 and 565.2 cm^{-1} correspond to stretching vibration of tetrahedral metal-oxygen bond; The Low intensity bands at 532.3, 449.3 and 400.0 cm^{-1} correspond to metal oxygen vibrations in octahedral sites. For an ideal spinel crystal, shallow absorption band corresponds to octahedral metal-oxygen vibrations and an intense absorption band results due to tetrahedral metal-oxygen vibrations. However, in real crystals undergo deviation from ideal crystal structure due to presence of cations with variable ionic radii. In an effort to accommodate cations with larger ionic radii, oxygen atoms are displaced from their ideal position in the lattice. An ideal spinel structure is represented by oxygen position parameter value 0.250. In this study, Rietveld refinement of X-ray diffraction pattern of $Mn_{0.8}Zn_{0.2}In_{0.100}Fe_{1.900}O_4$ resulted in higher value (0.262) of oxygen position parameter. This indicates substantial displacement of oxygen position parameter in order to accommodate various cations and hence the crystal structure has undergone lowering of symmetry. It is known that various silent IR modes could be activated in spinel ferrites and additional absorption bands may appear due to structural distortion and hence lowering of symmetry [14]. Activation of the silent IR modes is responsible for appearance of additional absorption bands in this work.

4. Conclusions

In^{3+} substituted Mn-Zn ferrites were successfully prepared by using oxalate co-precipitation technique followed by microwave heating. X-ray diffraction pattern was simulated by Rietveld refinement in order to confirm formation of single phase spinel structure and determine cation distribution at octahedral and tetrahedral sites. Substantial redistribution of cations is noted from the fit. Additional, absorption bands in FTIR spectra confirms lowering of crystalline symmetry; this is also corroborated by high value oxygen position parameter.

10. References

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