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Synthesis and Characterization of Lanthanum-doped Ni-Co-Zn Spinel Ferrites Nanoparticles via Normal Micro-Emulsion Method

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Abstract

La-doping Ni-rich nano ferro spinel compounds synthesized via normal micro-emulsion method. The characterization of the prepared ferrites by means of X-ray diffraction shows structural characterization of $Ni_{0.6}Co_{0.2}Zn_{0.2}Fe_{2-y}La_yO_4$, shows well defined cubic spinel structure with some secondary phase of ortho ferrite, $LaFeO_3$ is detected. FT-IR of the La^{+3} doped ferrites analyzed in the range of 4000-400 cm^{-1}. The absorption bands 'ν_1' and 'ν_2' are assigned to the intrinsic stretching vibrations of tetrahedral complexes and octahedral complexes respectively. Surface morphology studied by SEM and particle size determined by TEM.

Keywords: Nano Ferrites, Normal Micro-emulsion, XRD, IR.

1. INTRODUCTION

The nano ferro spinel compounds have been studied in these recent years for its technological application such as ferro fluids, magnetic chips, drug delivery, high density information storage etc. [1]. Rare earth ions-doped ferrites have significant importance and they appear to be a promising material for numerous industrial applications; therefore, rare earth ions play an increasingly important role as dopants [2]. The addition of rare earth metal ions changes in the structure and texture [3]. In this context, we have previously investigated the impact of the nonmagnetic La^{+3} substitutions on the crystal structure, microstructure and static magnetic properties of

Ni-Co and Ni-Co-Zn ferrites [4]. The normal micelles method used, because of low cost route, environmental protection, conveniently operated and excellent composition controlled method.

However, from literature survey it is observed that there is no work carried out the substitution of La^{+3} doped Ni-Co-Zn nano ferro spinel synthesized by normal micro-emulsion method. In the current work decided to study the effect of La^{+3} on the structural and magnetic properties of Ni-Co-Zn with a chemical formula $Ni_{0.6}Co_{0.2}Zn_{0.2}Fe_{2-y}La_yO_4$ (y=0.00 to 0.10 in the step of 0.025).

2. EXPERIMENTAL

Materials

The analytical grade reagent of Nickel nitrate ($Ni(NO_3)_2$.6H2O), Cobalt nitrate ($Co(NO_3)_2.6H_2O$), Zinc nitrate ($Zn(NO_3)_2.6H_2O$), Ferric nitrate ($Fe(NO_3)_3.9H_2O$), Lanthanum nitrate ($La(NO_3)_3.5H_2O$), Sodium Doceyl Sulphate (SDS) and Methyl amine (40% in water) used for the synthesis.

Synthesis of nanoparticles by normal micro-emulsion method

The normal micro-emulsion method, employed to prepare the samples having the chemical composition $Ni_{0.6}Co_{0.2}Zn_{0.2}Fe_{2-y}La_yO_4$ (y=0.00 to 0.10 in the step of 0.025). The AR grade corresponding metal nitrates were used as starting material and were mixed in a stoichiometric proportion in double distilled water. An aqueous solution of Sodium Doceyl Sulphate (SDS) added into metal nitrate mixture with continuous stirring at temperature 45 °C, Methyl amine (40% in water) added; up-to pH ≅ 9 at constant temperature. Dark brown precipitate formed and stirred for 3 hours at temperature 60 °C, and then precipitate digested for overnight. The precipitate filtered through Wattman filter paper No. 41, washed with double distilled water and dried at room temperature, resulting a brown coloured powder.

3. RESULTS AND DISCUSSION

XRD Studies

The nano ferrite of particles having composition $Ni_{0.6}Co_{0.2}Zn_{0.2}Fe_{2-y}La_yO_4$ (y=0.050) shows the XRD pattern as in Figure 1.

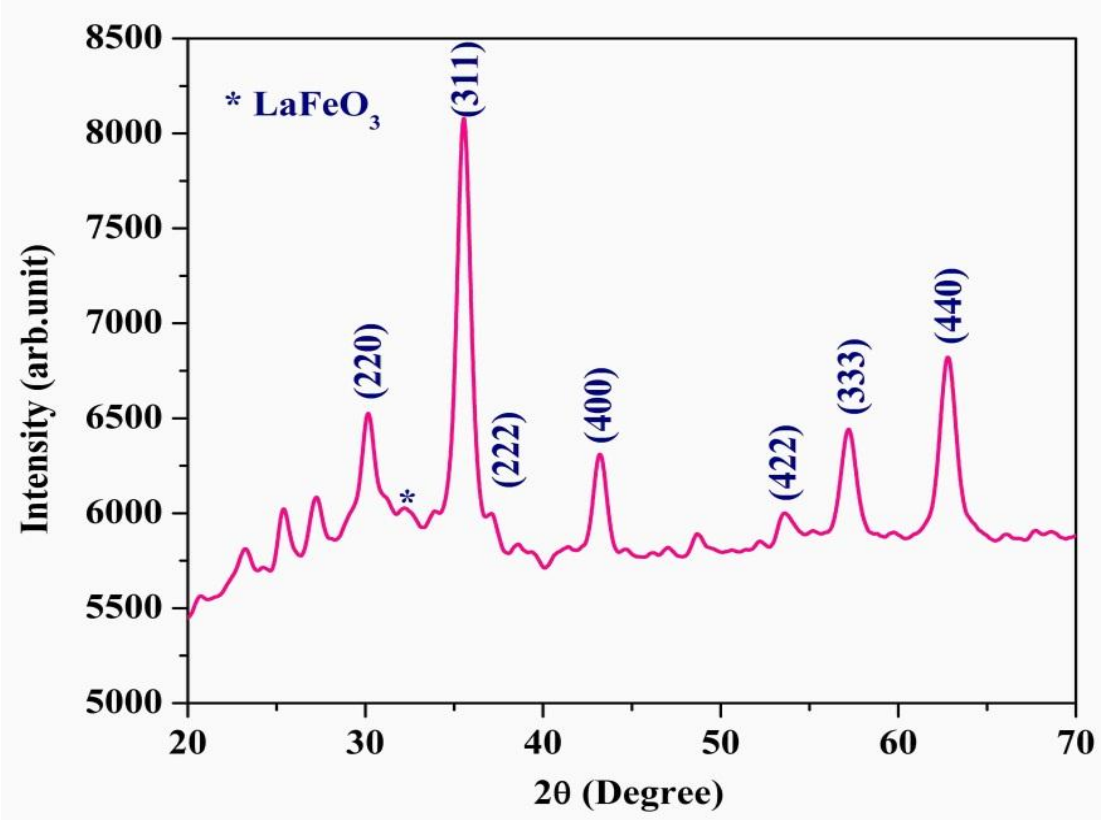

Figure 1: XRD spectrum of $Ni_{0.6}Co_{0.2}Zn_{0.2}Fe_{2-y}La_yO_4$ (y=0.050).

Peaks are observed; (220), (311), (222), (400), (420) and (440) indicates, single phase cubic spinel structure, with increase in peak of (311) due to increase in La^{+3} ions content [5]. The secondary phase detected ortho ferrite phase of $LaFeO_3$, also confirmed from JCPDS card number 75-0541.The crystal lattice is distorted when the defect concentration is too high, that further gives rise to the formation of the new phase compound. As a result, there was a limit for the replacement of Fe^{+3} with La^{+3} ions. Therefore, redundant La^{+3} ions form the $LaFeO_3$ on the grain boundaries [6]. Because the ionic radius of La^{+3} ions (1.05 Å) is larger as compared to that of Fe^{+3} ions (0.67 Å), the replacement of Fe^{+3} by La^{+3} is limited in the spinel lattice, redundant La^{+3} ions form $LaFeO_3$ on the grain boundaries [7].

FT-IR studies

The FT–IR spectrum is very useful technique to demonstrate the structural parameter. Figure 2 represents the IR absorption spectrum of the nano ferrite $Ni_{0.6}Co_{0.2}Zn_{0.2}Fe_{2-y}La_yO_4$(y=0.050).

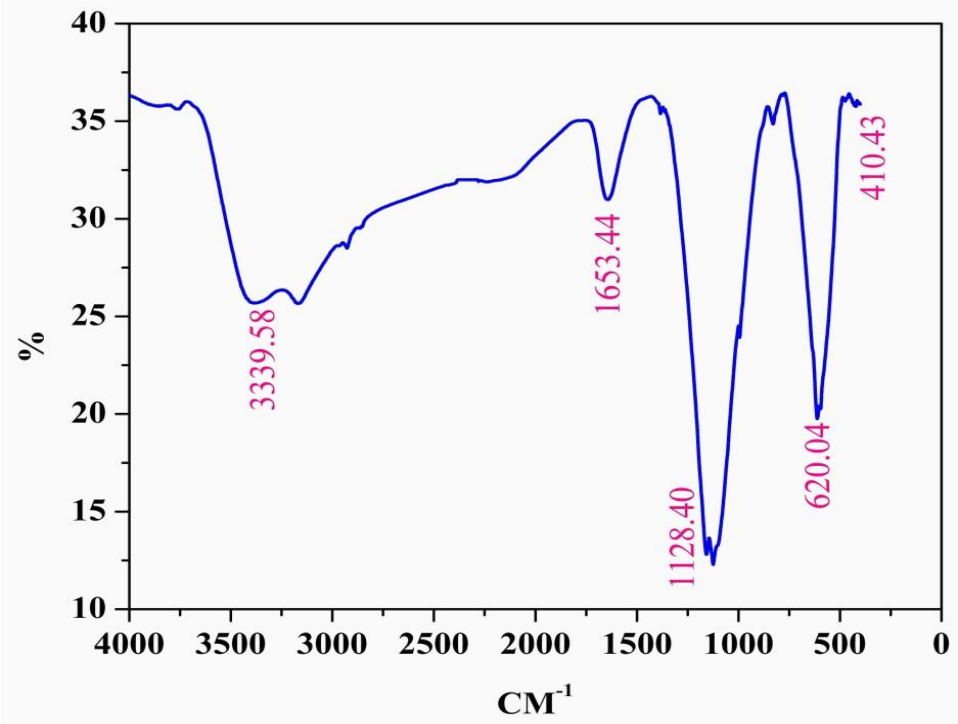

Figure 2: IR spectrum of $Ni_{0.6}Co_{0.2}Zn_{0.2}Fe_{2-y}La_yO_4$ (y=0.050).

The adsorbed water molecule is assigned by bands around 3400 and 1600 cm^{-1}, which are assigned to the O–H stretching and H–O–H bending modes of vibration, respectively [8]. The absorption band at 1130 cm^{-1} is assigned to be deformation of C-H group and carboxylic acid group [9].

The absorption bands 'ν_1' around 600-625 cm^{-1} and 'ν_2' around 400-425 cm^{-1} are assigned to the intrinsic stretching vibrations of tetrahedral complexes and octahedral complexes respectively. The presence of the above absorption bands corresponds to the metal-oxygen bonds in spinel ferrites. The absorption bands υ_1 and υ_2 are slightly shifts to higher frequency, due to addition of La^{+3} ions content. This shifts can attributed to the decrease in M-O bond length, band intensity and broadening of the A-sites and B-sites. The difference in the frequencies of υ_1 and υ_2 is due to the changes in bond length (Fe^{+3} - O^{-2}) at tetrahedral and octahedral sites [10].

SEM Studies

The SEM image of ferrite composition $Ni_{0.6}Co_{0.2}Zn_{0.2}Fe_{2-y}La_yO_4$(y=0.05). The Figure 3 shows that the La^{+3} doping basically improves the homogeneity of the grain size uniform distribution of particles. This is achieved through the diffusion of La^{+3} ions

mainly near the grain boundary, which creates ion and oxygen vacancies; thus, it controls the boundary mobility and may even facilitate sintering [11, 12].

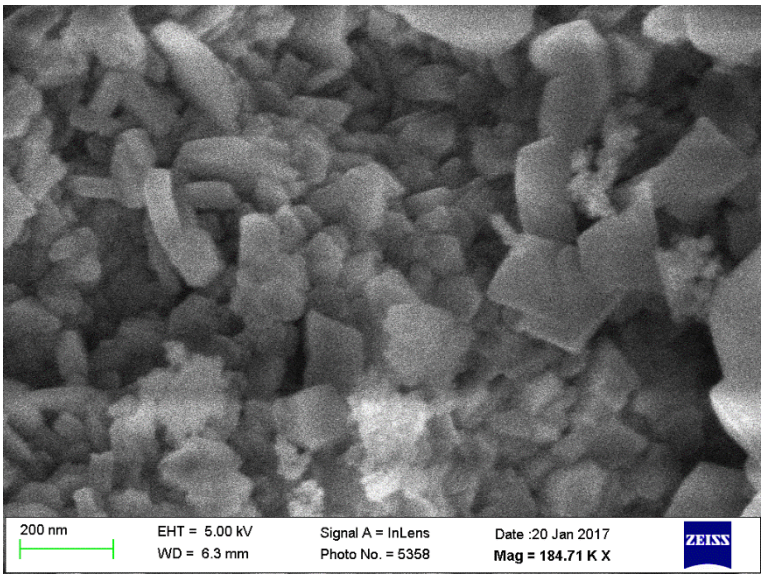

Figure 3: SEM image of $Ni_{0.6}Co_{0.2}Zn_{0.2}Fe_{2-y}La_yO_4$ (y=0.05).

TEM Studies

The TEM image of nano ferrite with composition $Ni_{0.6}Co_{0.2}Zn_{0.2}Fe_{2-y}La_yO_4$ (y=0.05) as shown in Figure 6. The particles good agreement with average crystalline size estimated by XRD around 20 nm. These two values confirm the formation the single crystal ferrite. It is observed that the particle well distributed and slightly agglomerated and is due to magneto statics interaction between the particles [13].

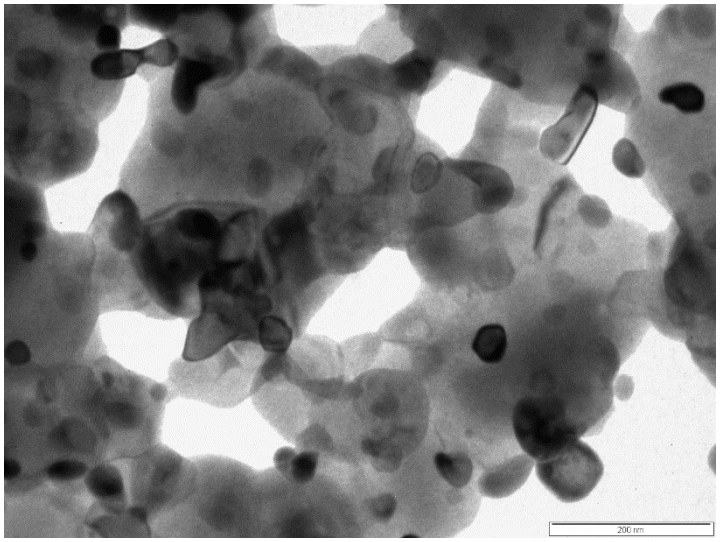

Figure 4: TEM image of $Ni_{0.6}Co_{0.2}Zn_{0.2}Fe_{2-y}La_yO_4$ (y=0.05).

4. CONCLUSION

O/W micro-emulsion method is used to prepare the La^{+3} doped nano ferrite chemical composition $Ni_{0.6}Co_{0.2}Zn_{0.2}Fe_{2-y}La_yO_4$(y=0.00, 0.025, 0.050, 0.075, 0.10). The XRD pattern reveals the formation of single-phase cubic spinel structure for all the compositions with some secondary phase. The IR shows two absorption bands 'ν_1' around 600-625 cm^{-1} is assigned to the intrinsic stretching vibrations of tetrahedral complexes and band 'ν_2' around 400-425 cm^{-1} is assigned as octahedral complexes. The average particle size was measured by TEM around 23 nm.

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