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RESEARCH ARTICLE

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SYNTHESIS AND CHARACTERIZATION OF $Ni_{0.5}Li_{0.5}Al_{0.5}Fe_2O_4$ (NLAF) SPINEL NANO FERRITES BY SOL-GEL METHOD

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ABSTRACT
The cobalt substituted Ni-Li-Al spinel nanoferrites with the general formula $Ni_{0.5}Li_{0.5}$ $Al_{0.5}Fe_2O_4$ (NLAF) was prepared using sol-gel method. Structural characterization of the samples was carried out using X-ray powder diffraction (XRD), FT IR, technique. The lattice parameter of the sample was found to be 10.7167Å .The surface chemistry and morphological characterization of the prepared sample was studied by Scanning Electron Microscopy (SEM) gives nanosized grains. Nanocrystalline shape and sizes of NLAF was also confirmed by Transmission Electron Microscopy (TEM). FT-IR absorption spectra show two prominent bands characteristics of A and B site vibrations. The crystallite size was in the range of 43 nm to 45 nm. Such low nano sized ferrites are desirable for variety of applications like in magnetic data storage and environmental applications.

1. Introduction

Ferrites are mixed oxides with general formula AB_2O_4, where A is a metal ion with +2 valence and B is the Fe+3 ion. Spinel compounds possess a cubic unit cell which can be regarded as built of eight smaller cubes called octants or formula units, corresponding to the formula of "A8B16O32". Accordingly, the spinel unit cell contains 32 oxide ions, 64 tetrahedral sites and 32 octahedral sites. In order to achieve a charge balance of the ions, the interstitial voids will be only partially occupied by positive ions. Therefore, in stoichiometric spinels, only one-eighth of the tetrahedral sites and one-half of the octahedral sites are occupied by metal ions. A common feature of the ferrite nanomaterials is that they usually adopt a mixed spinel structure, characterized by the presence of divalent (A^{2+}) and trivalent (Fe^{3+}) cations in both crystallographic sites. The wet chemical synthetic routes have proven to be much more advantageous for the preparation of transition metal ferrites than the physical methods since they provide a better control over the size, size distribution, shape, and degree of agglomeration of the resulting nanocrystals. Spinel ferrites play an important role in technological applications. Their interesting electrical, magnetic, and dielectric properties make them useful in many applications, such as electronic devices, sensors, memory devices, data storage, and telecommunications[1]. Recently, the possibility of preparing ferrites in the form of nanoparticles has opened a new and exciting research field with revolutionary applications, not only in electronic technology but also in the fields of biotechnology[2] and water treatment[3], due to their nanometer size, superparamagnetic properties, and a high surface-to-volume ratio[4]. In recent years, NPs have been applied for removing heavy metals and organic

pollutants from aqueous solutions[5]. Lithium ferrites have become significant materials with their high resistivity, low dielectric losses, high Curie temperature, square hysteresis loop properties. Due to which they are used as microwave devices like circulators, isolators, and phase shifters.[6] Lithium ferrites altered by substitution with metal ions like, cobalt (Co^{2+}), nickel (Ni^{2+}), zirconium (Zr^{4+}), zinc (Zn^{2+}) and titanium (Ti^{4+}), etc. have been widely studied by many workers.[7] Ferrites can be synthesized by various routes like highenergy ball milling,[8] sol–gel technique[9], etc.,

Examining the properties of nanoferrites is the most essential in the quickly developing zones like scientific, industries, design and research of nanotechnology. Ni– Al ferrite is a delicate attractive and an imperative ceramic material which has tremendous applications in different fields like electric, magnetic, electronics, microwave devices, catalysts, transformers cores, power conversions, high frequency applications in telecommunications, magnetically control drug delivery system, for multilayer inductor applications[10]. In this present work, we report for the synthesis of nanoparticles of $Ni_{0.5}Li_{0.5}$ $Al_{0.5}Fe_2O_4$ nanoferrite by simple sol-gel method using metal nitrates. The samples were characterized by, XRD, FTIR and TEM.

2.0 Experimental

2.1 Material and Method

All chemicals and solvents were AR grade or better purchased from Merck Co.Pvt Ltd and Sd. fine chemical used without any further purification. The stoichiometric amounts Citric acid $C_6H_8O_7$, ferric nitrate $Fe(NO_3)_3.9H_2O$ (99%), nickel nitrate $Ni(NO_3)_2.6H_2O$ (99.8%),– Al $(NO_3)_3$ $9H_2O$ (98%) and Lithium nitrate ($LiNO_3$) used as starting materials for the synthesis of NLAF spinel nanoferrites by sol-gel auto combustion technique.

2.2 Synthesis of nanoparticles

Required stoichiometric quantities of metal nitrates were dissolved in a minimum quantity of distilled water and mixed together. Aqueous solution of Citric acid was then added to the mixed metal nitrate solution. Ammonia solution was then added with constant stirring to maintain pH of the solution at 7.0. The resulting solution was continuously heated on the hot plate at 100°C up to dryness with continuous stirring. A viscous gel has resulted, increasing the temperature up to 250°C lead the ignition of gel. The dried gel burnt completely in a self propagating combustion manner to form a loose powder. The burnt powder was ground in Agate Mortar and Pestle to get a fine ferrite powder. Finally the burnt powder was calcinated in air at 750°C temperature for six hours and cooled to room temperature.

2.3 Characterization

2.3.1 X-ray Diffraction

The XRD analysis on the prepared samples was made using a SCINTAG X'TRA AA85516 (Thermo ARL) X-ray diffractometer equipped with a Peltier cooled Si solid detector. Monochromatized Cu K_α (λ = 1.5302 Å) was used as the radiation. Diffraction patterns were collected at 40 kV–35 mA, at 0.02°C step and count time of 0.400 sec over a range of 10.00–80.0 (2θ), at a step scan rate of 3.00 $min^{-1}$and the crystallite size (*D*) is calculated from X-ray line broadening of the (311)diffraction peak using the well-known Debye-Scherer's formula[11]:

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where β is the full-width at half-maxima of the strongestintensity diffraction peak (311), λ the wavelength of theradiation, and θ the angle of the strongest characteristicpeak.

X-ray density (ρ_x) was calculated using the following equation:

$$\rho x = \frac{8M}{Na^3}$$

Where *M* is the molecular weight (gm), N Avogadro's number(per mol)and *a* the lattice parameter in angstrom. The value of lattice parameter *a* determined from the high intense peak (311) of XRD pattern using the following equation[12] and values are given in Table 1.

$$a = \frac{d_{hkl}}{(\sqrt{h^2} + k^2 + l^2)}$$

where a is lattice constant d_{hkl} is inter-planar distance for *hkl* plane.

Table 1 Crystal Parameters of NLAF

Parameter	Value
Crystallite size (nm)	45.06
Lattice constant (Å)	10.7167
X-ray density (g cm^{-3})	8.1344

2.3.2 FTIR Spectroscopic Analysis

The adsorbents are examined using Fourier Transform Infrared spectroscopy (FTIR). The sample discs were prepared by mixing of 1 mg of powdered carbon with 500 mg of KBr (Merck-spectroscopy quality) in an agate mortar, then pressing the resulting mixture successively under a pressure of 5 tones/ cm^2 for about 5 min., and at 10 tones/ cm^2 for 5 min., under vacuum. The spectra were measured from 4000 to 400 cm^{-1} on a JASCO-FTIR-5300 model.

2.3.3 SEM analysis

The surfaces of the powder carbonaceous materials have been stubbed using the double-sided adhesive carbon tape. Samples are coated with the help of platinum coater [JOEL Auto fine coater model, JFC –1600 auto fine coater, Coating time is 120 sec with 20mA] and deposited with a thin layer of platinum on the sample. The microphotograph of prepared sample was recorded using SEM JEOL model, JSM-5600 an accelerating voltage of 5 kV, at high vacuum mode. The maximum magnification possible in the equipment is 3,00,000 times with a resolution of 3 nm, typically setting at various magnifications for all the samples of study.

2.3.4 Transmission electron microscopy (TEM) analysis

The ferrite sample was first sonicated (Vibronics VS 80) for 5 minutes. Ferrites were loaded on carbon coated copper grids, and solvent was allowed to evaporate under Infra light for 30 minutes. TEM measurements were performed on Phillips model CM 20 instrument, operated at an accelerating voltage at 200 kV. Hysteresis Tracer was employed to study the magnetic properties of the samples in the field of 10 kOe at room temperature.

3.0 Results and discussion

3.1 X-ray diffraction analysis: The XRD patterns of the sample $Ni_{0.5}Li_{0.5}Al_{0.5}Fe_2O_4$ (NLAF) shown in Figure 1.

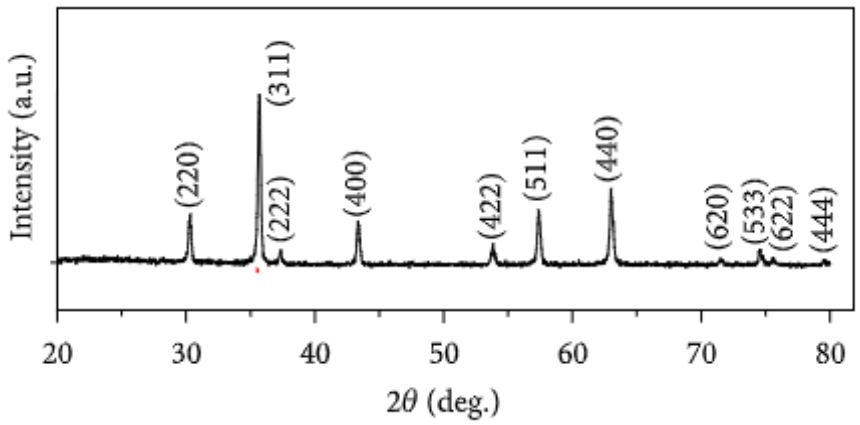

Figure 1: X-ray diffraction patterns of NLAF spinel Nanoferrites

The presence of the (220), (311), (222), (400), (422), (511), (440), (620), (533) (622) and (444) minor lattice planes in the XRD patterns agrees well with the powder diffraction of spinel cubic JCPDS file. All samples are considered to be single-phase spinel structure. The patterns indicate well-defined peaks of crystalline fcc phase which confirm spinel cubic structure of the sample. No any additional peaks corresponding to impurity phase were observed. The crystallite size (t) of the samples was calculated using Scherrer formula. The average crystallite size for the prepared samples has been calculated from the line broadening of the most intense peak (311) plane of the spinel structures using the Scherrer equation. The data on lattice constant 10.7167 Å, and x-ray density is 8.1344 (g cm^{-3}). All experimental peaks were matched with theoretically generated one and indexed. The average crystallite size has been found between 43.5 nm to 45.87 nm and on average 45.06 nm for nanosample prepared in the current study (Table1).

3.2 TEM analysis: Transmission electron microscopy the morphology and structure of the prepared ferrite samples calcinated at 750°C were investigated by TEM techniques as shown in Fig.2.

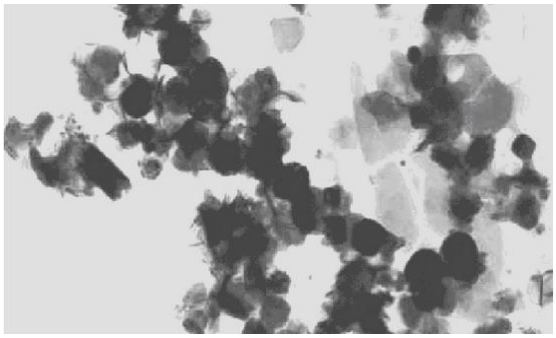

Figure 2: TEM image for NLAF nanoferrites calcinated at 750°C

The results indicate that the samples prepared by sol-gel method are almost uniform in both morphology and particle size distribution. A close inspection would reveal the presence of particles showing the spherical in shape. The particle sizes decreased with increasing Ni concentration. Mean particle size from TEM image is in good agreement with the crystallite size measured from X-ray line (311) broadening using scherrer's formula. This is lower than the particle size of nanoferrites prepared by other chemical method.

3.3 FT- IR Analysis: In the range of 800-400cm^{-1}, two main absorption bands were observed in the range of 604-542 cm^{-1} and 463-416cm^{-1}. These bands are attributed to the vibration of the tetrahedral and octahedral metal-oxygen (M-O) bonds in the lattices of the synthesized nanocrystals, respectively. These FTIR frequency bands for various Ni, Li and Al contents have been incorporated in the sample. FTIR spectra confirmed the formation of spinel cubic structure and the strong absorption bands with two characteristic peaks[13]. In ferrite sample the metal ions are situated at two sub lattices named tetrahedral (A) site and octahedral (B) site. The high frequency tetrahedral (υ_1) band was observed in the range of 605-636 cm^{-1} and low frequency octahedral band (υ_2) was observed in the range of 404-414 cm^{-1} and shown in Figure 3. This confirms the spinel structure of the prepared ferrite compositions. Similar reports were observed by Zahi and Pathak[14,15].

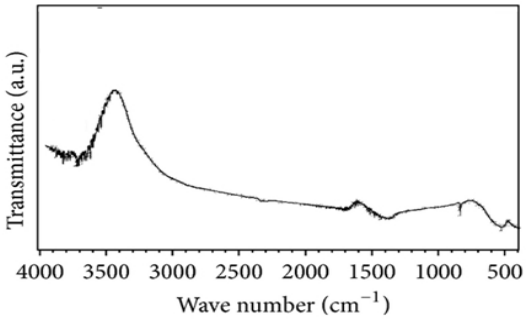

Figure 3: FTIR spectra of NLAF nanoferrites calcinated at 750°C

These two observed bands (□1 and □2) correspond to the intrinsic vibrations of tetrahedral and octahedral Fe^{3+}–O_2 complexes, respectively.

3.4 Surface Morphology by SEM: The surface morphology of the NLAF samples were studied using SEM(Scanning Electron Microscope). The secondary electron images are taken at different magnifications to study the morphology of samples by SEM. Fig(4) shows the SEM micro structures of the Aluminum doped Lithium Nickel nano ferrites. The images show that the particles have an almost homogeneous distribution, and some of them are in agglomerated form. It is evidenced by SEM images that the aggregation of particles lies in nanometric region. The particles were observed as uniform grains (in different SEM images) confirming the crystalline structure of NLAF nanoferrites which were detected by XRD studies. The formation of Fe_2O_4 was chemically favoured by heating during the synthesis where as final reaction was completed during the sintering where the pores between the particles were removed combined with growth and strong bonds by agglomeration. It can be seen from SEM micrographs of various compositions that the morphology of the particles is similar. They reveal largely agglomerated, well defined nanoparticles of the sample powder with inhomogeneous broader grain size distribution. Such broader size distribution is characteristic of mechanically activated nano sized particles. The agglomeration of particles is also because they experience a permanent magnetic moment proportional to their volume[16].

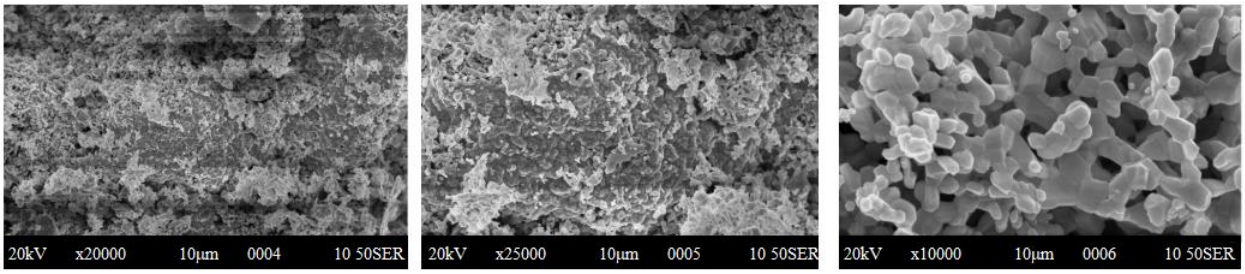

Figure 4: SEM images of NLAF nanoferrites calcinated at 750°C at different magnifications

Conclusions:

1. The Citrate-Gel auto combustion method to be a convenient method for obtaining homogeneous mixed NLAF nano ferrites without any impurity peak and material loss.
2. X-ray diffraction pattern confirm that the formation of single phase cubic spinel structure. The crystalline size of the nano ferrites in the range 43 to 45nm.
3. The distance between the magnetic ions on A and B calculated. It is clear that the distance between the magnetic ions decreases with increasing the Al content.
4. SEM analysis explains that the morphology of the particle is similar and particle sharpness is more or less spherical with some cluster/ agglomeration between the particles.

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