Preparation, Characterization and Electrical Properties Studies of Nano Sized Cerium Neodymium Doped Magnesium Ferrite

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Abstract

Nano crystalline magnesium Cerium Neodymium ferrite with general formula $MgCe_x$ Nd_y Fe_{2-x-y} O_4 (where x = 0.04, 0.06, 0.08, 0.10 and y=0.03,0.04,0.05,0.06) were prepared through sol-gel route from high purity nitrates of M agnesium (M g), Cerium(Ce), Neodymium(Nd) and Iron. The samples were sintered in microwave furnace and then characterized by XRD and SEM techniques. X-ray diffraction measurements confirmed the Nano size and formation of single phase cubic spinel structure of Magnesium ferrite. It was found that the lattice constant decreases with the increase in $Nd^{3+}Ce^{3+}$ concentration and the crystalline size of the samples was lying in the range of 53.22 – 53.74 nm, which was confirmed from the XRD studies. SEM studies show that the grain size of the samples decreases with the increase in Nd^{3+} Ce^{3+} content. This concludes that Nd^{3+} , Ce^{3+} occupies B-site.. The dielectric studies confirm the electrical behaviour and used to understand the electromagnetic properties of these nano ferrite materials. The permittivity studies show the decrease in relative permittivity of the ferrite material.

Keywords

Nanomaterials Sol-Gel, XRD, SEM Relative Permittivity.

I. INTRODUCTION

Magnesium ferrites have attracted much attention in recent years as one of the candidates for high density magnetic recording [1-5], microwave absorbents, sensors and electronic device, high frequency devices ,color imaging etc [6-8], because it has high magnetic permeability and high electrical resistance. Many research groups have investigated to enhance the electrical properties of magnesium ferrites Mg represents the divalent transition metal, hence the electrical properties of spinel ferrites can be varied systematically by changing the identity of the divalent Mg^{2+}cations without changing the spinel crystal structure [1]. It is well known that the chemical, structural, and electrical properties of spinel ferrites nano particles are strongly influenced by their composition and micro structures, which are sensitive to the preparation methodologies. Khan and Zhang [9] showed that the magnetic properties of Nano M gFe_2O_4 can be controlled by doping the spinel ferrite with lanthanide (Ce or Nd) up to the mole ratio of 0.12. The present work reports the influence of rare-earth ion (Ce-Nd) on the structural behaviour and electrical properties of $MgFe_2O_4$. These Magnesium ferrites were prepared by sol gel route [1] for maintaining low coercivity and low permittivity .

II.EXPERIMENTAL PROCEDURE

A) Synthesis Technique

Nanocrystalline powders of M g Ce_x Nd_y Fe_{2-x-y} O_4 (where x = 0.04, 0.06, 0.08, 0.10 and y=0.03,0.04,0.05,0.06) were prepared by sol-gel auto-combustion route. All the chemical used were of A.R Grade - Citric acid [$C_6H_8O_7.H_2O$] M erck, Ferric Nitrate [$Fe(NO_3)_3.9H_2O$]M erck, M agnesium nitrate[M $g(NO_3)_2.H_2O$] Lobo Chem., Cerium Nitrate [$Ce(NO_3)_2.H_2O$] Alfa Aesar and Neodymium nitrate [$Nd(NO_3)_3.XH_2O$] Alfa Aesar.The required amount of metal nitrates and citric acid are taken so as to have a molar ratio of 1:1 [1]. N and Ce atoms are substituted for Fe atoms at x and y ratio respectively, where as x is varied for 0.04, 0.06, 0.08, 0.10 and y was taken as y=0.03, 0.04, 0.05, 0.06 and dissolved in 100 ml of deionized water. The required amount of ammonia solution was slowly added to adjust the pH to 7. The mixed solution was heated and burnt on a hot plate with continuous heating at a temperature of 92˚C. The viscous brown gel burnt with glowing flints. The auto ignition was completed within a minute, yielding into a brown-colored ash. The as-prepared powders of all the sample were sintered in a microwave furnace VBCC/M F to a temperature of 750˚C for 1.5 hours [10]. The grain size of the nanoferrite was determined using Scherrer's equation. The FWHM value of the peak corresponding to a plane was considered after correction for instrumental broadening.

B) XRD Studies

To study the phase and crystallinity of the nano material XRD studies were performed on PAN analytical X'pert PRO

C) SEM Studies

Scanning Electron microscope (SEM) micrographs of the nano ferrite substrate was recorded using a scanning electron microscope (HITACHI model S-3000H). These SEM

micrographs were used to estimate the nano size of the material particles

D) Electrical Measurements

The Electrical measurements were performed using the N4L LCR meter (PSM 1735). The experimental set up for measuring the dielectric properties in the microwave region consisted of a pallet holder connected to the N4L LCR meter interfacing the computer [11]. The microwave properties of the four samples Ce(x)-Nd(y) doped magnesium ferrite x = 0.04, 0.06, 0.08, 0.10 and y=0.03,0.04,0.05,0.06) were investigated at the frequency range from 20 KHz to 20 MHz

III. RESULTS AND DISCUSSION

A) X-ray diffraction

The broader peaks of XRD indicated the fine crystalline size of the ferrite powder and the phase formation behaviour of M g Ce_x Nd_y Fe_{2-x-y} O_4 in the XRD Fig 1. As the Figure.1 shows the X-ray diffraction patterns of as burnt ferrite powder of different composition of M g Ce_xNd_y Fe_{2-x-y} O_4, The XRD patterns were similar to the JCPDS card number 89-3084 for magnesium ferrite powder and peaks of Ce and Nd are marked in the XRD, which are in accordance to JCPDS card number 75-0161. The figure confirms the absence of metal oxide phase in the as burnt powder. The X-ray pattern shows reflection plane (220), (311), (222) (400), (422), and (440). It was also observed that the appearance of plane (222) is there in all the sample patterns, which clearly indicates the presence of $MgFe_2O_4$ in single-phase cubic spinel structure.

The secondary phase (orthorhombic) was also observed due to the presence of rare-earth ortho-ferrite ($CeFeO_3$). The presence of secondary phase also suggest the solubility limit of Ce^{3+} ions in the spinel lattice due to its radius (0.083 nm, 0.095 nm, and 0.115 nm) [12].It was well known that the degree of replacement of the host cations by the other ions in the host lattice depending on the cations radius of the substituent [13]. The lattice constant *a* (A°) in the spinel structure are mentioned in Table 1 had been calculated from the prominent peak (311) by using Bragg's equation:

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

Table 1: XRD, Cation distribution of $MgCe_xNd_yFe_{2-x-y}O_4$

Sample		Lattice constant(A^o)	Crystalline Size(nm)
X	Y		
0.04	0.03	0.03	8.542
0.06	0.04	0.04	8.519
0.08	0.05	0.05	8.516
0.10	0.06	0.06	8.515

h, k, l are the indices of the mentioned planes. Lattice constants of all samples prepared in investigation are listed in Table 1. The lattice constant is smaller than pure $MgFe_2O_4$ and increases with the addition of C_e and N_d ions. This is attributed to the large difference between cation radii of R^{3+} and Fe^{3+} owing to the removal of rare-earth ions from the spinel lattice. The size of crystal was evaluated by measuring the FWHM of the most intense peak (311) mentioned in Table 1 using the Debye Scherrer's formula [14].

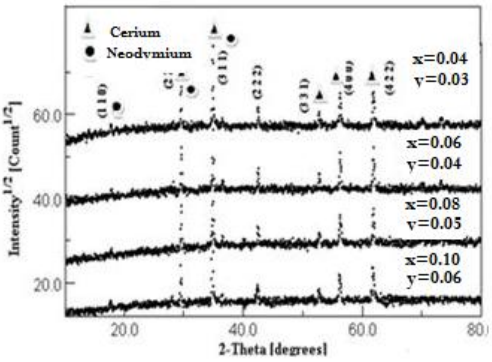

Fig1 XRD patterns of sintered Mg Ce_x Nd_y Fe_{2-x-y} O_4 ferrite with different C_e-N_d content x=0.04, 0.06, 0.08,y=0.03,0.04,0.05,0.06.

$$D = \frac{0.94\,\lambda}{\beta\,COS\;\theta}$$

B) SEM analysis

SEM Fig. 2, 3, 4 and 5 show the microstructure of sintered specimen. The Unsubstituted speci-men Fig 2 showed the presence of a monophasic homogeneous microstructure with an average grain size 0.42 nm in the encircled region [2-5].Where as Ce- Nd doped specimen's Fig 3-5 show a bi-phasic microstructure constituted of dark ferrite matrix grains and small whitish grain at the grain junction/boundary (encircled region), according to Sattar et, al [2] the rare earth ions occupy either the iron positions or go to the grain boundaries. However we have to exclude the probability that the rare earth ions occupy the B- site of Fe^{3+} ions. This is due to the fact that the tetrahedral sites are small to be occupied by the large rare earth ions which have large ionic radius. Of course the probability of occupancy in the octahedral site (B-site) by the rare earth ions will increase with in decrease in ionic radius R. The grain size of matrix phase was maximum in $x^{1/4}$ 0.016 composition Fig 5. Here the relatively lower grain size of ferrite matrix was in $x^{1/4}$ 0.018 compositions may be due to the grain growth inhibition caused by Ce-Nd FeO_3 seen in Fig 3-5, as compared to Fig 2.

The grains in the unsubstituted sample are inhomogeneous [1] i.e., the grains are affected by certain stress, while the grains for the Ce-Nd substituted Mg Ferrite samples are nearly homo-geneous due to the decrease of stress. The

photographs confirm these results that the stability has increased for the substituted samples.

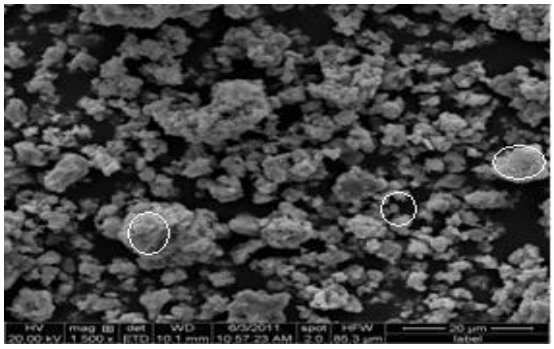

Fig.2 $MgFe_2O_4$

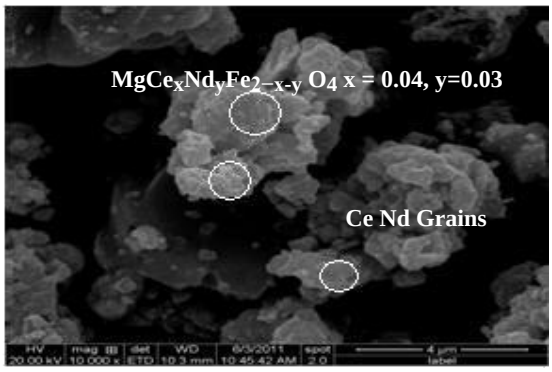

Fig.3 $MgCe_xNd_y Fe_{2-x-y}O_4$ x = 0.04, y=0.03

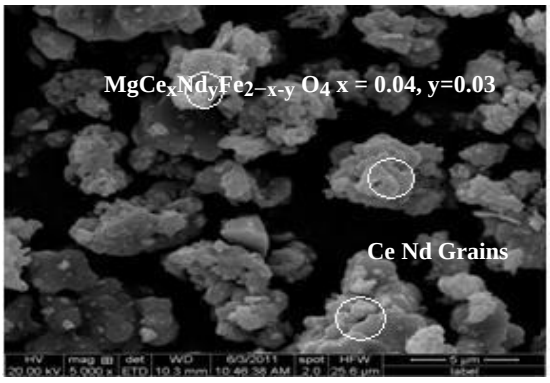

Fig.4 $MgCe_xNd_y Fe_{2-x-y}O_4$ x=0.06,y=0.04

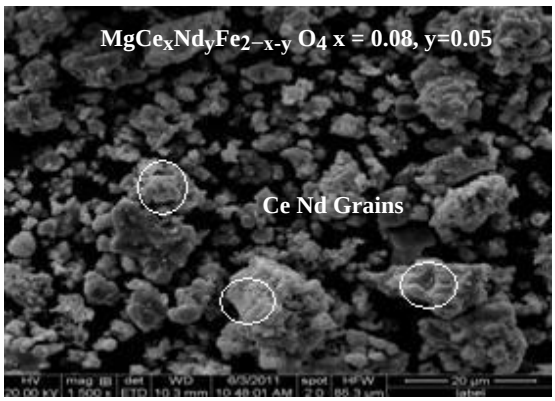

Fig.5 $MgCe_xNd_y Fe_{2-x-y}O_4$ x=0.08,y=0.05

D) Electrical Properties

The dielectric constant of the sintered samples (Mg $Ce_xNd_yFe_{2-x-y}$ O4 x=0.04, 0.06, 0.08, 0.10 and y=0.03,0.04,0.05,0.06) over the microwave frequency range from .02M –.02GHz are shown in Fig 6.The maximum value of dielectric constant 2.334, was observed for the sample x=0.04 and minimum was 1.7398 for the sample, x=0.10.

The high value of dielectric constant of the sample x=0.04 as compared to x=0.10 may be explained on the basis of the structural changes associated with the magnesium ferrite when the grain size is reduced to nanometer order[10].. Magnesium ferrite crystallizes into a cubic close-packed arrangement of oxygen ions. It belongs to the class of ferrites with an inverse spinel structure having structural formula, $Fe^{3+}[Mg^{2+}Fe^{3+}Ce^{3+}Nd^{3+}]O_4$ [15]. The metal ions given in the square bracket are called octahedral (B site) ions and that outside the square bracket are called tetrahedral (A site) ions. The magnesium ions ($Ce^{3+}Nd^{3+)}$ together with half of the iron ions (Fe^{3+}) occupy the B site [16] and the remaining half of the iron ions reside in A site. The presence of Ce^{3+} and Nd^{3+}ions gives rise to p -type carriers (holes) where as Fe^{2+} and Fe^{3+} ions produce n-type carriers (electrons). Therefore, both electrons and holes that are present in the B sites are due to the presence of Nd and Fe ions. Since only iron ions are present in A sites, electrons are the carriers in A sites [17].

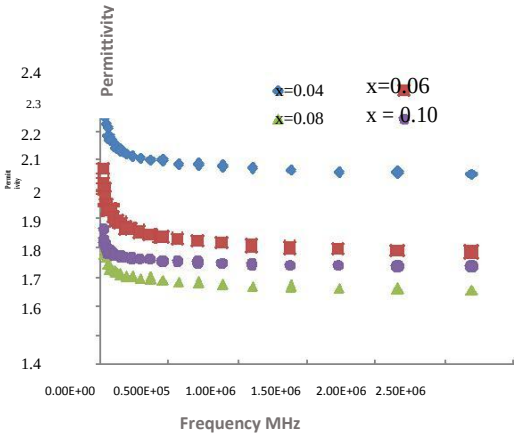

Fig.6 Permittivity study for $MgCe_x Nd_y Fe_{2-x-y} O_4$ x=0.04,0.006,0.08,0.10 y=0.03,0.04,0.05,0.06.

The distance between the ions in A sites (0.357 nm) is larger than the distance between the ions in B site (0.292 nm) . Also, the degree of covalence for the A site ions is higher than that of the B site ions. All the above factors result in a high activation energy for the A sites compared to the B sites. Hence, in ordinary magnesium ferrite with an inverse spinel structure the electron movement in B sites dominates compared to that in A sites. In Fig.6 it has been observed that the value of relative

permittivity (ε_r) decreases with the increase in Ce concentration, this shows that the prepared material Ce-Nd doped $MgFe_2O_4$ can be used for constructing microstrip patch antenna (MSPA).

IV. CONCLUSION

From the above experimental results, it is clearly evident that the nano size of the ferrite particles can be obtained from sol-gel route and which was found to be very simple and more efficient for the synthesis of Ce, Nd doped Magnesium ferrites. The nanocrystalline $MgCe_x\ Nd_y\ Fe_{2-x-y}\ O_4$ ferrite powders were successfully synthesized with different doping. The phase purity, crystallite size and particle size of the prepared ferrites was confirmed by XRD and SEM micrographs. The dielectric constant and loss tangent of the ferrites were determined by using LCR meter. It is found that the maximum and minimum value of dielectric constant for $MgCe_x\ Nd_y\ Fe_{2-x-y}\ O_4$ ferrites is 2.33 and 1.73 respectively which causes relative permittivity to be decrease with the increase in Ce-Nd. Further note that the dopant concentration should be increased further to decrease the relative permittivity (εr) of Ce-N_d doped $MgFe_2O_4$.From the above features it may be concluded that the prepared ferrites samples are the suitable candidate material for designing and developing the Microstrip patch antenna. This change will be also suitable for reducing the size of the antenna.

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