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Synthesization of Cerium Doped Nano Zinc Cobalt Ferrite for Voc Sensor Studies

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ABSTRACT: The magnetic properties of Zn-ferrite ceramics Zn_{1-x-y} Co_y Ce_x Fe $_2O_4$, (where x =0.012, 0.014, 0.016, 0.018 and y = 0.001, 0.001, 0.014, 0.016) were synthesized by sol gel auto combustion method. The structure and composition of Ce doped Zn-ferrite ceramics was analyzed and the nano size was confirmed by the SEM monographs. The VSM studies confirm the magnetic behaviour and used to understand the electromagnetic properties of these nano materials.

Key words: Ferrimagnetic materials; Nanomaterials; Magnetization, VSM, SEM

I. INTRODUCTION

In advanced technologies the ferrites are used for magnetic or electrical applications, as they are the required high-density materials [1-3]. Synthesis of nanometer size particles proved to be one of the interesting fields of material science in material processing and technological applications, as the small size particles have some of the interesting properties as compared to bulk particles. These particles have improved catalytic, dielectric and magnetic, properties, as they possess high resistivity and negligible eddy current losses [4]. Magnetic nano particles promise some interesting applications, such as in high frequency devices, magnetic fluids, high density magnetic recording, colour imaging etc[5-9]

The various processing techniques, which are used for the synthesis of spinel ferrite powders include microwave refluxing[10] , sol-gel[11], hydrothermal[12], co-precipitation [13], spray pyrolysis[14]. In fact there are numerous papers on synthesis of Zinc ferrite by various methods. In the present investigation we have employed sol-gel auto-ignition method to synthesize Ce doped Zinc ferrite nanoparticles. The sol-gel auto-ignition method is used to speed up the synthesis of complex materials. It is a simple process, which offers a significant saving in time and energy consumption over the traditional methods, and requires less sintering temperature. This method is employed to obtain improved powder characteristics, more homogeneity and narrow particle size distribution, thereby influencing structural, electrical, and magnetic properties of spinel ferrites. We examined the microstructures of the end products by X-ray diffraction and SEM to obtain quasi-three dimensional information on the grain shape, size and pore sizes[15]. It has been already reported that Zinc ferrite is an n type semi conductor with a band gap of 3.37eV[16-17]. Cerium-substituted ferrite, in particular, has been found to exhibit a large magneto-optic effect and low propagation loss, which will be good candidate materials for the devices with higher quality [18,19]. A low coercivity, high-remanence, soft magnetic material, having a hysteresis loop, is required for microwave operation. For a magnetic material to be applied in microwave devices, the most important static magnetic properties are the saturation magnetization (Ms), anisotropy constants, Neel temperature, remanent magnetization, coercivity (Hc). In general, Ms and Hc are required for applications [20].

II. EXPERIMENTAL PROCEDURE

2.1 Synthesis Technique

Nanocrystalline powders of Zn_{1-x-y} Co_y Ce_x Fe $_2O_4$, (where x =0.012, 0.014, 0.016, 0.018 and y = 0.001, 0.001, 0.014, 0.016) were prepared by sol-gel auto-ignition method. The metal nitrates were dissolved together in a minimum amount of de-ionized water to get a clear solution. An aqueous solution of citric acid was mixed with metal nitrates solution, then ammonia solution was slowly added to adjust the pH to 7. The mixed solution was moved on to a hot plate with continuous stirring at 94˚C. The viscous brown gel burnt with glowing flints. The auto ignition was completed within a minute, yielding into brown-colored ash. The as-prepared powders of all the samples were sintered in a microwave furnace

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VBCC/MF to a temperature of 600˚C for 1.5 hours. The grain size of the nanoferrite is determined using Scherrer's equation. The FWHM value of the peak corresponding to plane was considered after correction for instrumental broadening. Using the knowledge of site preference of the ions and the ionic size data of the respective ions, the cation distribution has been estimated theoretically using the following formula proposed [21, 22]. Mentioned in Table.2

$$\eta = \frac{M_W \times M_S}{5585}$$

Where M_W is the molecular weight of the sample and Ms is the saturation magnetization in emu/g.

2.2 FTIR study

Infrared absorption spectra in the range of 3.72×10^4 m^{-1} to 5.43×10^4 m^{-1} were recorded at room temperature by using SHIMADZU FTIR spectrum one spectrometer using KBr pellet method. The spectrum transmittance (%) against wave number (m^{-1}) is used for interpretation of the results.

2.3 SEM Studies

Micrographs of the sensor were recorded using a scanning electron microscope (HITACHI model S-3000H).

2.4 Magnetic Measurements

The Magnetic measurements were performed using the commercial vibrating sample magnetometer (VSM) Lakeshore (Model73009). Magnetic hysteresis loops were measured at room temperature with maximal applied magnetic fields up to 0.95T. Magnetic field sweep rate was 5 Oe/s for all measurements, so that the measurement of hysteresis loops with maximum field of 0.989 T took about three hours.

III. RESULTS AND DISCUSSION

3.1 SEM analysis

Fig. 1 shows the microstructure of sintered specimen. Unsubstituted specimen (Fig.1) shows the presence of a monophasic homogeneous microstructure with an average grain size 0.42nm.Whereas, Ce-doped specimens' show a bi-phasic microstructure constituted of dark ferrite matrix grains and small whitish grain at the grain junction/boundary. As proposed by Sattar et, al [23] .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 of the octahedral (B-site) by the rare earth ions will increase with decrease in the R ionic radius. This indicated whitish grains were CeFeO3.

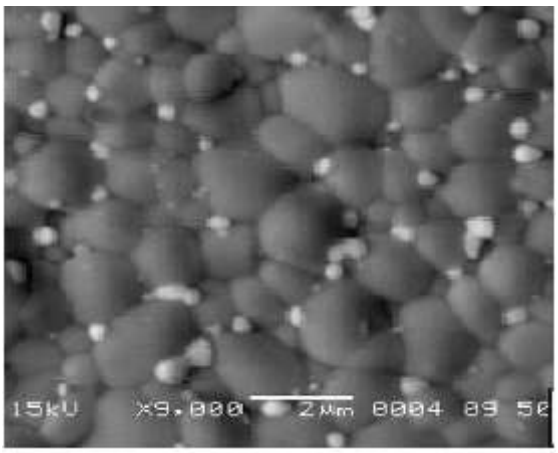

Fig.1 Zn_{1-x-y} Co_yCe_x Fe_2O_4 x=0.016,y=0.014

The grains in the unsubstituted sample are inhomogeneous i.e., the grains are affected by certain stress, while the grains for the Fe substituted sample are nearly homogeneous due to the decrease of stress. The photographs confirm these results that the stability increased for substituted samples.

3.2 Hysterisis studies

Fig. 3,4 shows the variation in saturation magnetization (Ms) for the different x values of Zn $_{1-x-y}$ Co_y Ce_x Fe $_2O$ $_4$ ferrite, the saturation magnetization (Ms) value increases with in increase in the value of x in Table.1.

The increasing Cerium content induced a polar-to-nonpolar phase transition. Within the polar region, a rhombohedral and two orthorhombic modifications of Zn $_{1-x-y}$ Co_y Ce_x Fe $_2O$ $_4$ were

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found. It was shown that Cerium substitution resulted in the appearance of spontaneous magnetization, which was significantly enhanced upon the composition-driven transition from a rhombohedral to an orthorhombic phase.

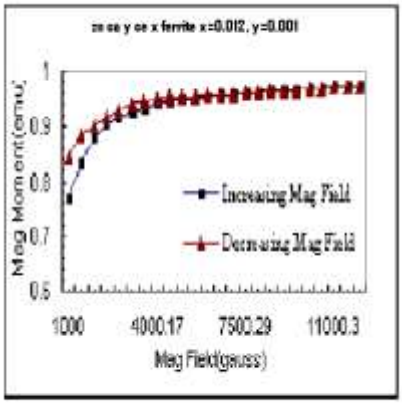

Fig.2 Zn_{1-x-y} Co_yCe_x Fe_2O_4 x=0.012,y=0.001 Saturation magnetization (Ms)

Table 1 show that the change in retentivity and change of coercive force with change in concentration respectively. The coercive force show linear increase initially and later shows a gradual decrease with the increase in the dopant concentration. The values of magnetic parameters such as M_S, H_C, M_R of nano particles of Zn_{1-x-y} Co_y Ce_x Fe $_2O_4$ obtained from the VSM data are 25.0 emu/gm,723.24G, 11.507 emu/gm respectively. As reported [24,25] M_s value for bulk particle of $ZnFe_2O_4$ as 27 emu/g . Therefore the increase in saturation magnetization can be attributed to the effect of nano regime on it. The difference in the value of M_S can be explained in the light of cation distribution. Any change in the concentration and nature of the ions in A and B site should cause resultant magnetization to be different from reported one [26].

3.3. FTIR study

The study of far-infrared spectra is an important tool to get the information about the position of ions in the crystal [27]. FTIR absorption spectra of the samples in the range of 3.5×10^4 m^{-1} to 5.8×10^4 m^{-1} are given in Fig. 9. The spectra show two major absorption bands in the given frequency range. The high and low frequency absorption bands (υ_1, υ_2) are observed in a frequency range of 5.59×10^4 m^{-1} to 5.73×10^4 m^{-1} and 3.54×10^4 m^{-1} to 4.11×10^4 m^{-1}, which is attributed to tetrahedral and octahedral complexes Fe^{3+}–O^{2-} These two bands have been reported by Waldron in spinel structure of ferrite. No shift of absorption band υ_1 is observed. The absorption band υ_2 is slightly shifted to a higher frequency side with addition of R ions and is attributed to increase in bond length on the B-site [28]. This suggests that the rare-earth ions occupy the B-site. The difference in frequencies between υ_1 and υ_2 is due to changes in bond length (Fe^{3+}–O^{2-}) at tetrahedral and octahedral sites.The broadening of the υ_2 band is observed in rare-earth added $ZnFe_2O_4$, which suggests the occupancy of rare-earth ions on the B-sites .

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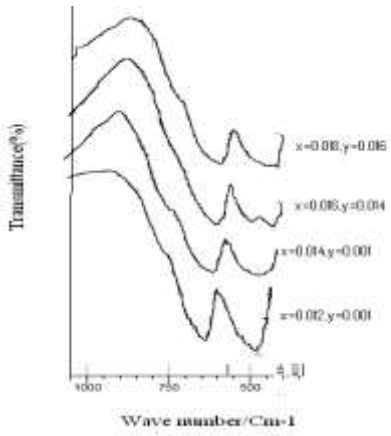

Fig.3 FTIR absorption spectra of the samples.

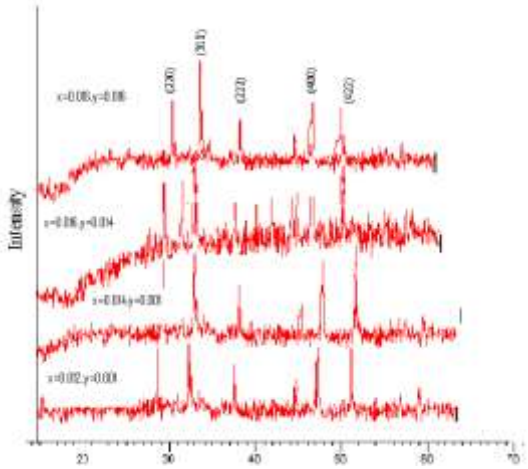

Fig.4 XRD patterns of sintered Zn_{1-x-y} Co_y Ce_x Fe $_2O_4$, ferrite with different Ce content x =0.012, 0.014, 0.016, 0.018 and y = 0.001, 0.001, 0.014, 0.016)

3.4 X-ray diffraction.

Fig.4. shows the X-ray diffraction patterns of pure $ZnFe_2O_4$ and x of cerium ions added to $ZnFe_2O_4$. The X-ray pattern shows reflection plane (220), (311), (222) , (400), (422), and (440). It was observed that the appearance of plane (222) is there in all the sample patterns clearly indicate that the pure $ZnFe_2O_4$ shows the presence of single-phase cubic spinel structure. The secondary phase (orthorhombic) is observed in rare-earth ions added Cerium ferrites. The observed secondary phase includes rare earth orthoferrite $CeFeO_3$. It is well known that the degree of replacement of the host cations by the other ions in the host lattice depends on the cations radius of the substituent .The lattice constant a (nm) of spinel structure could be calculated for prominent peak (311) using Bragg's equation

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

Where hkl are the indices of mentioned planes.

Lattice constants of all samples prepared in investigation are listed in Table 2. The lattice constant is smaller than pure ZnFe2O4 and increases with the increase in radius of Ce ions. This is attributed to the large difference between cation radii of R3+ and Fe3+ owing to the removal of rare-earth ions from the spinel lattice.

The size of crystallite was evaluated by measuring the FWHM of the most intense peak (311) by the Debye Scherrer formula .

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

XRD patterns exhibit narrow reflection that points to the narrow size crystallites. The results are as shown in Table.2 the mean crystallite

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size of the sample lies in the range of 48.38 nm to 76.98 nm. The crystallite size of R ions added sample is smaller than pure Zinc Ferrite.

IV. CONCLUSION

From the above experimental results, it is clearly evident that the nano size of the ferrite particles has caused increase in magnetization in Ce doped $ZnFe_2O_4$. Since Saturation magnetization and coercive force increases with the increase in Ce, these parameters will be very useful for the application of the ferrite materials in the Sensor Studies.

$Zn_{1-x-y}Co_yCe_xFe_2O_4$		Ms (emu)	Mag. Mom.	Coercivity (G)	Retentivity (emu)
X=0.012	Y=0.001	0.0769	0.00333	392.95	0.0033
X=0.014	Y=0.001	0.1539	0.00667	147	0.026
X=0.016	Y=0.014	0.214	0.00928	124	0.037
X=0.018	Y=0.016	0.2488	0.0108	155	0.056

Table 1 and 2 shows Ms, Magnetic moment, G, Lattice constant and particle size , Absorption (ν_1 ν_2) .

Zn_{1-x-y} Co_y Ce_x Fe_2 O_4	Lattice Constant(a□ A□	Particle size(D) nm	Absorption/cm^{-1} ν_1	Absorption/cm^{-1} ν_2
X=0.012, y=0.001	8.32515	76.98	372.25	349.09
X=0.o14, y=0.001	8.34459	72.57	381.88	347.16
X=0.016, y=0.014	8.32638	66.96	385.74	362.59
X=0.018, y=0.016	8.342	48.38	383.81	543.89

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