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MODIFICATION IN STRUCTURAL AND ELECTRICAL PROPERTIES OF COBALT FERRITE NANOPARTICLES BY TITANIUM SUBSTITUTION

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ABSTRACT

Nowadays the magnetic nanoparticles gained much interest of researchers due to their wide range of applications on account of their smaller size and large surface to volume ratio. Hence, the present investigations deal with the effect of substitution of tetravalent (Ti^{4+}) ion in cobalt ferrite matrix on structural and electric properties. The samples with generic formula $Co_{1+x}Ti_xFe_{2-2x}O_4$ (x=0.00, 0.10, 0.30 and 0.50) were prepared in nanocrystalline form using the standard sol-gel autocombustion technique by taking citric acid as a fuel. The prepared nanoparticles were characterized by X-ray diffraction (XRD) technique.The twoprobe technique was employed to measure the electric properties of the investigated samples.The XRD spectra confirm the cubic spinel structure of the samples without any impurity and particle size obtained by Scherrer's formula gives confirmation of nano size of synthesized samples. The Arrhenius plots show semiconducting behavior of all the samples and the DC resistivity improved by substitution of tetravalent (Ti^{4+}) ion in cobalt ferrite. The requirements of electronic industry may fulfil with the synthesized nanoparticles. The increased DC resistivity in cobalt ferrite with Ti^{4+} substitution can be useful for the energy storage applications.

Keywords*: Ferrite, Nanoparticles, XRD, DC resistivity*.

I. INTRODUCTION

WITH The magnetic materials have playinga crucial role in the daily life because of their useful properties. Among the magnetic materials, the polycrystalline ferrites have been paid special attention due to their chemical stability as well as their excellent combination of electrical and magnetic properties. On the basis of their high electrical resistivity, low eddy current and dielectric losses, high saturation magnetization and high permeability these materials have been employed in many technological areas[1, 2].Spinel ferrite with cubic spinel structure possesses two interstitial sites namely, tetrahedral (A) site and octahedral [B] site. The metal cations reside at tetrahedral and octahedral sites depending upon their ionic radii and crystal field stabilization energy [3].

Spinel ferrites with the chemical formula MFe_2O_4 (where, M = divalent cations like Co, Ni, Cu, Mn, Mg, Cd, Zn,etc) are the most promising materials as they find widespread applications in several areas including antenna rod, transformer core, memory chips,etc[4]. These applications mostly belong to bulk spinel ferrites. Spinel ferrites can be prepared in thin film form as well as in nanosize form to have applications in different areas.

In the recent years, intense research has been carried out on nanosize spinel ferrites due to the high surface to volume ratio, which makes them useful in the applications of the field of imaging and therapy, drug delivery, catalyst,etc. [5]. The important applications of spinel ferrites are due to the accommodation of a variety of cations at their interstitial sites, tetrahedral (A) and octahedral [B] sites. The divalent[6], trivalent[7] and tetravalent[8] cation can also be incorporated in spinel lattice to bring out variation in electrical and magnetic properties.

Among these magnetic nanoparticles, cobalt ferrite with a cubic spinel structure, has gained its prominence due to its high coercivity (Hc), moderate saturation magnetization (Ms), good chemical stability and high mechanical hardness. In literature the properties of cobalt ferrites modified mostly by substituting divalent cations[9, 10]. The effect of substitution of tetravalent ions in cobalt ferrites on the basic electrical and magnetic properties has not been reported much in the literature.

In the present work, the structural and electrical properties were investigated for titaniumsubstituted cobalt ferrite $Co_{1+x}Ti_xFe_{2-2x}O_4$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5). Titanium is mainly used as a refractory and opacifier, although it is used in small amounts as an alloying agent for its strong resistance to corrosion. The $CoFe_2O_4$ and TiO_2in nano size are found very useful in various technological applications, so the present investigated samples may beuseful in many technological applications.

II. EXPERIMENTAL METHOD

Synthesis

Ti^{4+} substituted cobalt ferrite nanoparticles of chemical formula $Co_{1+x}Ti_xFe_{2-2x}O_4$ (x=0.00, 0.10, 0.20, 0.30, 0.40 and 0.50) were synthesized by using sol-gel auto combustion method. AR grade chemicals such as tetrabutyl titanate ($C_{16}H_{36}O_4Ti$), cobalt nitrate ($Co(NO_3)_39H_2O$), ferric nitrate ($Fe(NO_3)_39H_2O$) as oxidants and citric acid ($C_6H_8O_7{\cdot}H_2O$) as fuelwere used. The metal nitrates to fuel ratio were chosen as 1:3 by adopting the propellant chemistry. Ethanol (C_2H_6O) was used as a solvent to dissolve tetrabutyl titanate while ammonia solution was used to adjust the pH at 7. The reaction was carried out at a temperature of 90°C. The details of sol-gel auto combustion synthesis method are reported in our previous report[11]. The as-prepared powder was sintered at 650°C for 6h to remove any impurity of nitrate remained and for well crystal growth. The sintered powder was used for structural, characterizations and for electrical measurements the powders were pressed into circular pallets and used for the measurements.

Characterizations

The sintered powder of typical samples was characterized by X-ray diffraction technique. X-ray diffraction patterns of typical the samples were recorded at room temperature by using a Regaku Miniflex-II X-ray powder diffractometer operated at 40 kV and 30 mA. The diffraction patterns were recorded in the 2θ range 20^0 to 80^0 with a scanning rate of 2^0 per minute using Cu-K_α radiation of wavelength 1.5406 Ǻ.The DC resistivity of the synthesized nanoparticles was measured by two probe technique.

III. RESULTS AND DISCUSSION

Structural properties

The X-ray diffraction (XRD) technique was used to characterize the prepared samples of $Co_{1+x}Ti_xFe_{2-2x}O_4$. All the XRD pattern shows well-defined reflections belonging to cubic spinel structure. Typical XRD pattern of the sample x = 0.00 and 0.40 is shown in Fig.1 and 2 respectively.All the peaks in the XRD pattern were indexed by using Bragg's law. The presence of planes (220), (311), (222), (400), (422), (511) and (440) in the XRD pattern reveals the cubic spinel structure of all the samples. It is also evident that all the peaks are intense and sharp. No impurity peaks were observed. Thus the samples are single phase in nature. The peaks get broader with the substitution of Ti^{4+} ions. Similar results were reported in the literature for XRD patterns of titanium substituted lithium ferrite [12].
The intensity of (311) plane is more as compared to other planes like (220), (222), (400), (422), (511) and (440). The Lattice constant (a) values of the titanium substituted cobalt ferrite nanoparticles were calculated using standard relation [13] and found to increase with substitution. The obtained values of the lattice constant (a) are tabulated in table 1. The increase in lattice constant with titanium content x can be interpretedon the basis of the ionic radii of the constituent ions Co^{2+}, Ti^{4+}, Fe^{3+}. The substitution of Ti^{4+} with Co^{2+} ions in place of two Fe^{3+} ions leads to increase in lattice constant. Similar behavior of lattice constant was reported in the literature for spinel ferrite[14].

The particle size of the titanium substituted cobalt ferrite powders was calculated by using the most intense peak (311) and using the Debye-Scherrer relation,and it was found in nanometre range for all the samples, which confirms the nano crystallite size of synthesized samples.

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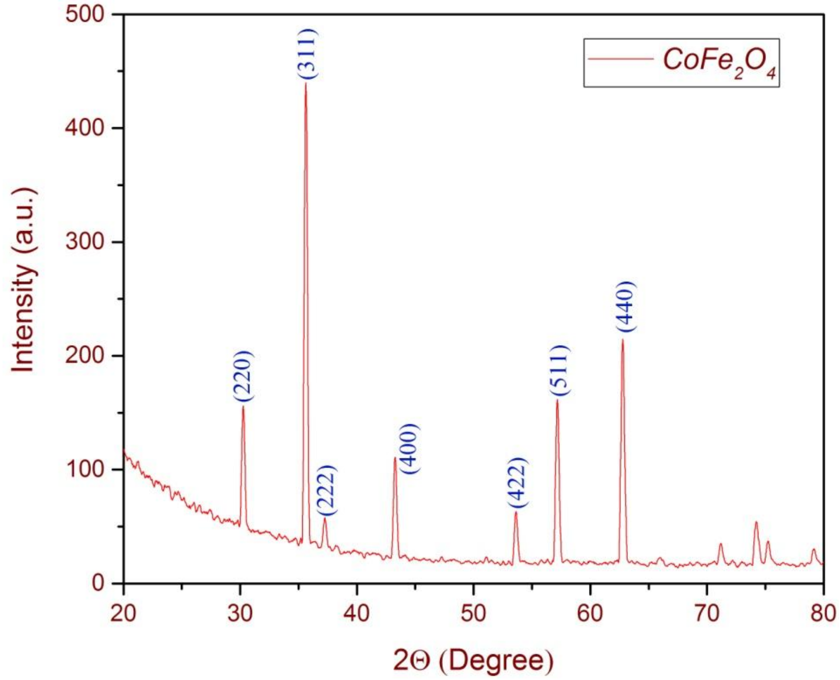

Fig.1: Typical XRD pattern of $Co_{1+x}Ti_xFe_{2-2x}O_4$(x = 0.00)

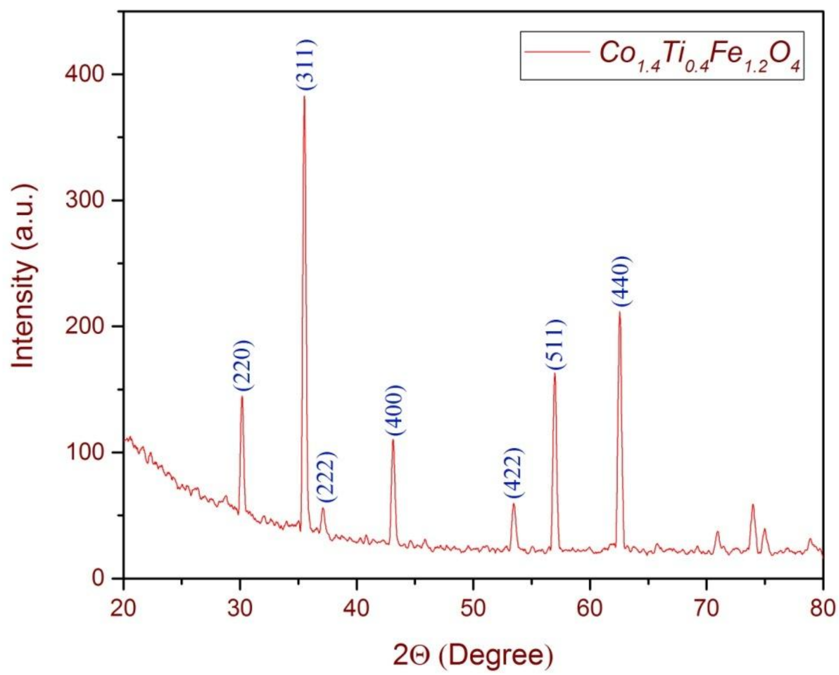

Fig.2: Typical XRD pattern of $Co_{1+x}Ti_xFe_{2-2x}O_4$(x = 0.40)

Using XRD data various structural parameters such as Hopping length (L_A, L_B), tetrahedral bond length (d_{AL}), octahedral bond length (d_{BL}), tetra edge (d_{AE}) and octa edge (d_{BEU}) shared and unshared were evaluated from standard relations [15] and listed in Table 1.

All the values reported in Table 1 are compatible with those reported for cobalt ferrite nanoparticles in the literature [16, 17]. The values of hopping lengths, i.e., the distance between magnetic ions increase with the nonmagnetic substitution in present series of spinel ferrite [18]. The bond lengths at the tetrahedral and octahedral site, also the tetra and octa edge were found to increase after the substitution of Ti^{4+} at the place of Fe^{3+} ions.

Table 1. lattice parameter (a), hopping length (L_A, L_B), tetrahedral bond length (d_{AL}), octahedral bond length (d_{BL}), tetra edge (d_{AE}) and octa edge (d_{BEU}) shared and unshared and average crystallite size (t) of $Co_{1+x}Ti_xFe_{2-2x}O_4$ nanoparticles

x	a (Å)	L_A	L_B	d_{AL}	d_{BL}	d_{AE}	d_{BEU} Shared	d_{BEU} Unshared	t (nm)
0.00	8.365	3.622	2.958	1.898	2.042	3.100	2.816	2.959	37
0.40	8.385	2.529	2.450	1.902	2.047	3.107	2.822	2.966	36

Electrical properties

Themeasurements of DC resistivity 'ρ' for all the samples of the $Co_{1+x}Ti_xFe_{2-2x}O_4$ferrite system were carried out in the temperature range 300-800 K using standard two probe method. The D.C. electrical resistivity plots of all the samples are shown in figure3.It is clear from the resistivity plots that the electrical resistivity of all Ti^{4+} substituted cobalt spinel ferrite samples decreases with increase in temperature, thus exhibiting semiconducting behavior obeying the well-known Arrhenius relation. It is also seen from figure 3that there are two regions of conduction with different activation energies. The change in slope is observed in each resistivity plot at a particular temperature which may correspond to Curie temperature of the sample. The increase in conductivity with Ti^{4+} substitution may be due to the hopping of electrons between Fe^{2+} and Fe^{3+}.

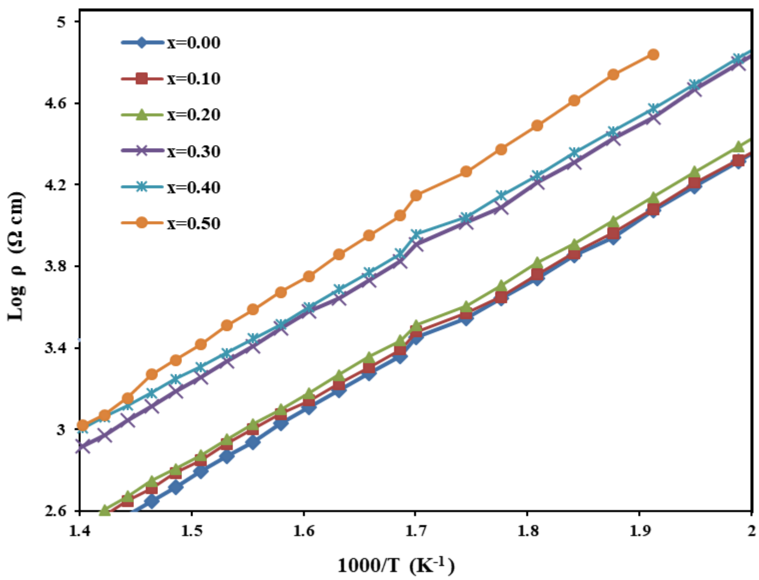

Fig. 3: Variation of dc electrical resistivity with reciprocal of temperaturefor $Co_{1+x}Ti_xFe_{2-2x}O_4$

IV. CONCLUSION

The nanocrystalline $Co_{1+x}Ti_xFe_{2-2x}O_4$ of different compositions with x = 0.0, 0.1, 0.2, 0.3, 0.4 and 0.5were successfully prepared by sol-gel auto-combustion technique using citric acid as a fuel and AR grade metal nitrates.

The X-ray diffraction results showed the formation of single phase cubic spinel structure. The crystallite size, the lattice constant,andall structural parameters are in the reported range. The crystallite size confirms thenanocrystalline nature of the samples. The substitution of titanium ions in cobalt ferrite results in an increase of electrical properties in general.The DC resistivity of all the samples decreases with increase in temperature exhibiting the semiconducting behavior. Overall the improved electrical properties of cobalt ferrite by tetravalent substitution may useful in electronic and energy storage device applications.

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