

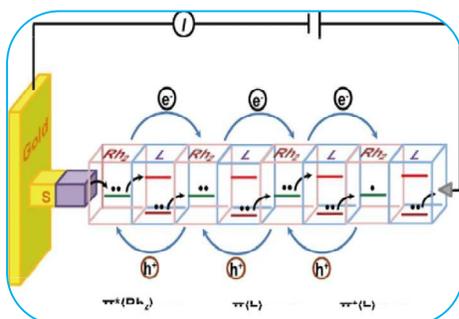


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Sol-gel synthesized ferrite nanoparticles of Ho^{3+} doped lithium ferrite were characterized by various techniques to study the hopping mechanism and d.c. electrical conductivity. Room temperature X-ray diffraction patterns confirms the cubic spinel structure of the samples with (311) peak as a most intense peak. The nano-scale dimension of the samples is confirmed by using X-ray diffraction data and also by using scanning electron micrographs. The hopping lengths are obtained from XRD data shows increasing trend with Ho^{3+} addition in lithium ferrite. The values allied parameters, such as distance of oxygen ion from A and B site cations (d_{AX} and d_{BX}), tetrahedral and octahedral (shared and unshared) edge (d_{AXE} , d_{BXE} and d_{BXEU}) are obtained by using the values of oxygen positional parameter and lattice constant. Two-probe technique is employed to measure the d.c. electrical resistivity of all the samples as a function of temperature. The decrease in the dc electrical resistivity with temperature may be due to the increase in hopping of electrons between Fe^{2+} and Fe^{3+} ions at the octahedral sites.

KEYWORDS: Sol-gel, hopping lengths, allied parameters, d.c. resistivity.

INTRODUCTION

Ferrite materials at nano-scale dimension shows very interesting and unique structural, chemical, electrical, mechanical, and magnetic properties with a verity of promising technological applications in high - density recording devices, color imaging, ferrofluids, high frequency devices and magnetic refrigerators. Recently the scientific community focused on

the study of substituted ferrite nano-particles synthesized via different routes. The electrical resistivity of lithium ferrite strongly affects the electrical and magnetic properties [1]. However, these properties are also susceptible to the purity of starting materials, calcination temperature and time, calcination atmosphere etc. [2]. Spinel ferrite nanoparticles in particular pure and substituted lithium ferrites shows remarkable advantages make them useful in microwave and memory core applications. Lithium ferrites are the low cost

materials possesses high resistivity and low losses of eddy current [3].

The synthesis route and nature of substituted cation modifies the structural magnetic and electric properties of ferrites. Sol-gel [4], wet-chemical co-precipitation [5], hydrothermal [6], mechano-chemical [7], refluxing [8], precursor [9], and auto-combustion [10] are the different synthesis routs discussed in literature which are used to obtain the ferrites at nano-scale dimension. To obtain the nano-particles of ferrite materials and homogeneous mixture of multi-

SOL-GEL SYNTHESIS, HOPPING MECHANISM AND D.C. ELECTRICAL RESISTIVITY IN LITHIUM FERRITE NANOPARTICLES DOPED BY Ho^{3+} ions

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ABSTRACT:

Sol-gel synthesized ferrite nanoparticles of Ho^{3+} doped lithium ferrite were characterized by various techniques to study the hopping mechanism and d.c. electrical conductivity. Room temperature X-ray diffraction patterns confirms the cubic spinel structure of the samples with (311) peak as a most intense peak. The nano-scale dimension of the samples is confirmed by using X-ray diffraction data and also by using scanning electron micrographs. The hopping lengths are obtained from XRD data shows increasing trend with Ho^{3+} addition in lithium ferrite. The values allied parameters, such as distance of oxygen ion from A and B site cations (d_{AX} and d_{BX}), tetrahedral and octahedral (shared and unshared) edge (d_{AXE} , d_{BXE} and d_{BXEU}) are obtained by using the values of oxygen positional parameter and lattice constant. Two-probe technique is employed to measure the d.c. electrical resistivity of all the samples as a function of temperature. The decrease in the dc electrical resistivity with temperature may be due to the increase in hopping of electrons between Fe^{2+} and Fe^{3+} ions at the octahedral sites.

elements at atomic or molecular level, sol-gel auto-combustion technique is the best option. Substituted lithium ferrites are useful materials for power applications due to their tailored magnetic and electrical properties [11-12]. The materials with high density and defect free fine grains are the requirements for microwave applications [13]. In the present study our main purpose is to study the hopping mechanism and d.c. electrical resistivity in Ho^{3+} substituted lithium ferrite nanoparticles obtained by sol-gel technique.

EXPERIMENTAL:

In order to obtain the homogeneous nano-powders of $\text{Li}_{0.5}\text{Fe}_{2.5-x}\text{Ho}_x\text{O}_4$ ($x = 0.0, 0.025, 0.050, 0.075$ and 0.1) at low temperature, sol-gel auto-combustion technique is employed. A. R. grade nitrates of constituent elements with high purity were used as initial materials. Citric acid was used as chelating agent by taking the molar ratio 1:3 with metal nitrates and the reaction was carried out in air atmosphere. The metal nitrates and citric acid mixed together and dissolved in distilled water as to obtain the clear solution. The liquid ammonia is poured slowly in the mixture and maintained the pH of the solution at 7. The whole mixture is kept on hot plate with magnetic stirrer at a constant temperature of 80°C . After some time the evaporation process starts and the water molecules were removed from the solution which in results in a dark brown viscous gel. After removal of all the water molecules from the liquid mixture the auto ignition process starts and the gel is burnt with glowing flints. The auto-ignition process was completed within few minutes and the brown-colored fine powders are obtained as a yield product. These powders were the sintered at temperature 700°C for 4 h.

The sintered powders are grinded in agate mortar pestle to obtain the fine particles and then subjected to X-ray diffraction investigations. The XRD patterns of all the samples are performed at room temperature by using Phillips X-ray diffractometer (Model 3710) using $\text{Cu-K}\alpha$ radiation with incident wavelength $\lambda = 1.5405 \text{ \AA}$. To study the d.c. electrical resistivity, all the samples are converted in to right circular disc shaped pellets with dimensions 10 mm in diameter and 1-3 mm in thickness. Silver paste is applied on the both circular faces of pellets as to make the good ohmic contact between surface of pellet and electric probes. The d.c. electrical resistivity of all the samples was recorded in the temperature range 300 – 800 K by using two probe method.

RESULTS AND DISCUSSION:

The X-ray diffraction technique is used to study the structural parameters viz. lattice parameter, X-ray density, particle size, hopping lengths and cation distribution etc. Room temperature XRD pattern taken in the 2θ range $20\text{-}70^\circ$ for the middle sample 0.050 is shown in Figure 1.

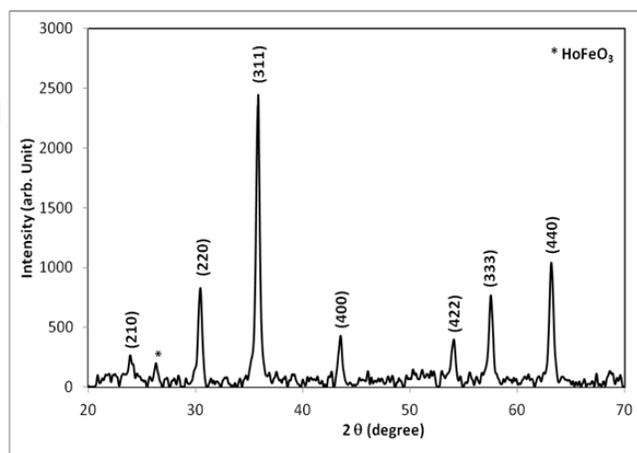


Figure 1: X-ray diffraction pattern for middle sample ($x = 0.05$) of $\text{Li}_{0.5}\text{Fe}_{2.5-x}\text{Ho}_x\text{O}_4$

The XRD pattern shown in Figure 1 confirms the single phase cubic spinel structure of a space group of Fd3m. The main reflection planes (210), (220), (311) (400), (422) (333), and (440) of the spinel structure are appeared in the XRD pattern. Ho³⁺ addition in lithium ferrites affects the single phase and an un-indexed secondary peak of HoFeO₃ is appeared. The sharp and broad nature of most intense peak (311) reveals the nano-crystalline nature of the samples.

The distance between magnetic ions (hopping lengths) in tetrahedral – A and octahedral B-site i.e. L_A and L_B respectively are given by the following relation;

$$L_A = \frac{a\sqrt{3}}{4}$$

$$L_B = \frac{a\sqrt{2}}{4}$$

Figure 2 shows the relation between the hopping lengths in octahedral (A) and tetrahedral [B] sites as a function of Ho³⁺ substitution in Li ferrite and the values are given in Table 1. The distance between magnetic ions increases as Ho³⁺ substitution increases. This may be due to the fact that, both 'L_A' and 'L_B' are directly proportional to lattice parameter which increases with Ho³⁺ addition. This change may also be attributed due to the ionic radii difference of the constituent ions, which makes the magnetic ions larger to each other and the jump lengths increases.

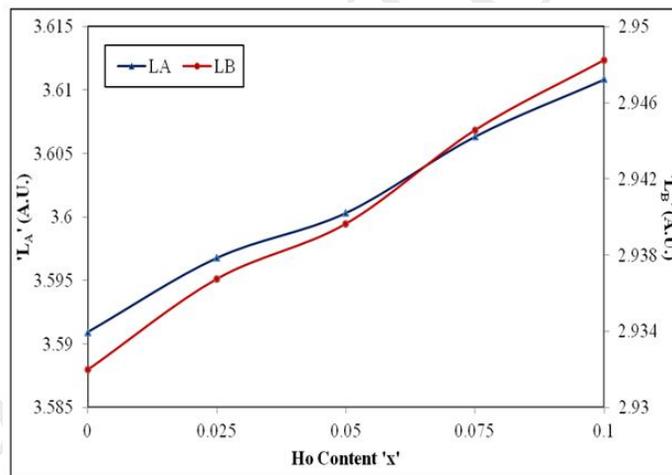


Figure 2: Variation of hopping lengths 'L_A' and 'L_B' for Li_{0.5}Fe_{2.5-x}Ho_xO₄

Table 1: Hopping lengths (L_A and L_B), allied parameters (d_{AX}, d_{BX}, d_{AXE}, d_{BXE}, and d_{BXEU}) for Li_{0.5}Fe_{2.5-x}Ho_xO₄

'x'	Hopping Lengths		Allied Parameters				
	L _A (Å)	L _B (Å)	d _{AX}	d _{BX}	d _{AXE}	d _{BXE}	d _{BXEU}
0.00	3.591	2.932	1.8723	2.0299	3.0574	2.8065	2.9333
0.025	3.597	2.937	1.8711	2.0355	3.0554	2.8180	2.9380
0.050	3.600	2.940	1.8703	2.0389	3.0543	2.8250	2.9408
0.075	3.606	2.945	1.8691	2.0448	3.0523	2.8368	2.9456
0.1	3.611	2.948	1.8682	2.0491	3.0508	2.8457	2.9491

The shortest distance between A-site cation and oxygen ion (d_{AX}) and the shortest distance between B-site cation and oxygen ion (d_{BX}), tetrahedral edge (d_{AXE}), shared octahedral edge (d_{BXE}) and unshared octahedral edge (d_{BXEU}) can be calculated by taking the values of lattice parameter 'a', oxygen positional parameter 'u' of each sample and by using the following relations [14];

$$d_{AX} = \sqrt{3} \left(u - \frac{1}{4} \right) a \quad 3$$

$$d_{BX} = \left(3u^2 - \frac{11u}{4} + \frac{43}{64} \right)^{1/2} a \quad 4$$

$$d_{AXE} = \sqrt{2} \left(2u - \frac{1}{2} \right) a \quad 5$$

$$d_{BAX} = \sqrt{2} (1 - 2u) a \quad 6$$

$$d_{BXEU} = \left(4u^2 - 3u + \frac{11}{16} \right)^{1/2} a \quad 7$$

All the values calculated by using above equations (3-7) are given in Table 1. It is observed from Table 1, that the bond length of tetrahedral edge ' d_{AX} ' slightly decreases whereas the bond length of octahedral edge ' d_{BX} ' increases with Ho^{3+} substitution. This is because the Ho^{3+} ions having larger ionic radii replaces Fe^{3+} ions with smaller ionic radii and occupy octahedral - B site only, so the octahedral site expands and tetrahedral site shrinks a little.

DC electrical resistivity for all the samples was measured by the two-probe method as a function of temperature and the results are shown in the form of plots of $\text{Log } \rho$ against inverse of absolute temperature and is shown in Figure 3. Resistivity decreases continuously with the increase in temperature, revealing the semiconducting nature of the prepared samples. The temperature dependence of resistivity found to follow the Arrhenius equation. The relation between resistivity and temperature may be expressed as,

$$\rho = \rho_0 \exp \left(\frac{\Delta E}{kT} \right) \quad 8$$

where, ρ is the dc electrical resistivity at temperature T, ρ_0 is the pre-exponential factor with the dimensions of $\Omega\text{-cm}$, k is the Boltzmann constant ($8.6173439 \times 10^{-5} \text{eV/K}$), ΔE is the activation energy, and T is the absolute temperature.

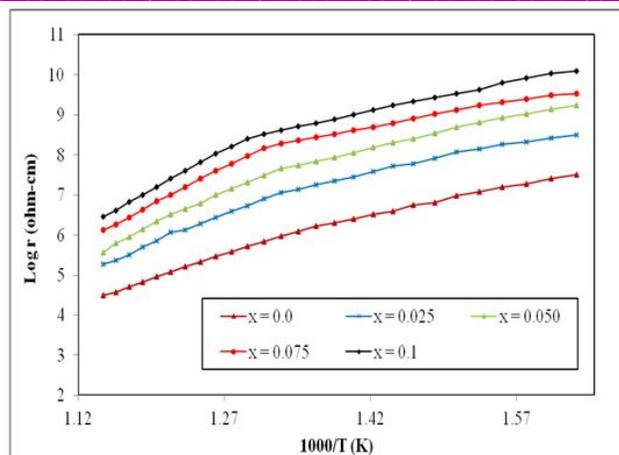


Figure 3: Variation of Log ρ versus $1000/T$ for $\text{Ho}_x\text{Li}_{0.5}\text{Fe}_{2.5-x}\text{O}_4$ ferrite system.

The decrease in the dc electrical resistivity with temperature may be due to the increase in hopping of electrons between Fe^{2+} and Fe^{3+} ions at the octahedral sites. The results are in accordance with the Verwey mechanism of conduction [15]. The presence of Ho^{3+} ions on B-sites increases the resistivity and favors the conduction mechanism. With increasing Ho^{3+} ions concentration, activation energy (ΔE) and resistivity increase. This can be explained by the fact that the trivalent Ho^{3+} ions, which are substituted for Fe^{3+} ions, prefer octahedral positions and instead of contributing to the conduction process, hamper the degree of conduction and thus increase ΔE and resistivity. Increase in Ho^{3+} substitution may produce an exotic metallic state near the insulator-metal transition as realized presently by the control of the band filling in 3d transition metal oxide compounds with strong electron correlation and canting [16].

CONCLUSIONS:

Sol-gel auto-combustion method is incorporated for the preparation of $\text{Li}_{0.5}\text{Fe}_{2.5-x}\text{Ho}_x\text{O}_4$ nanoparticles at low temperature. The main reflection planes (210), (220), (311) (400), (422) (333), and (440) of the spinel structure are appeared in the XRD pattern which confirms the cubic spinel structure with appearance of HoFeO_3 as secondary phase. The difference in ionic radii of constituent ions makes the size of magnetic ions larger and results in increasing the hopping lengths. The decrease in the dc electrical resistivity with temperature may be due to the increase in hopping of electrons between Fe^{2+} and Fe^{3+} ions at the octahedral sites.

REFERENCES:

- [1] M. V. Chaudhari, R. H. Kadam, S. B. Shelke, S. E. Shirasth, A. B. Kadam, D. R. Mane Powder Technology 259 (2014) 14-21.
- [2] S. K. Gurav, S. E. Shirsath, R. H. Kadam, D. R. Mane; Powder Technology; 235 (2013) 485-492.
- [3] S. E. Shirsath, R. H. Kadam, M. L. Mane, Ali Ghesami, Y. Yasukawa, X. Liu, A. Morisako; J. Alloy. Comp. 575 (2013) 145-151.
- [4] S. E. Shirsath, R. H. Kadam, A. S. Gaikwad, A. Ghesami, A. Morisako, J. Magn. Mater. 323 (2011) 3104-3108.
- [5] S. M. Patange, S. E. Shirsath, B. G. Toksha, S. S. Jadhav, K. M. Jadhav, J. Appl. Phys. 106 (2009) 023914.
- [6] B. Bruwati, R. K. Rana, S. V. Manorama, J. App. Phys. 101 (2007) 0143021
- [7] H. Yang, X. Zhang, W. Ao, G. Qui, Mater. Res. Bull. 39 (2004) 833
- [8] X. D. Li, W. S. Yang, F. Li, D. G. Evans, X. Duan, J. Phys. Chem. Solid. 67 (2006) 1286.
- [9] M. M. Hessian, J. Magn. Mater. 320 (2004) 2800.

- [10] B. G. Toksha, S. E. Shirsath, M. L. Mane, S. M. Patange, S. S. Jadhav, K. M. Jadhav, J. Phys. Chem. C 115 (2011) 20905.
- [11] Y. P. Fua, C. S. Hsu, Solid State Commun. 134 (2005) 201-206.
- [12] V. Verma, S. P. Gairola, V. Pandey, J. S. Tawale, H. Su, R. K. Kotnala, J. Magn. Magn. Mater. 321 (2009) 3808.
- [13] N. Gupta, M. C. Dimri, S. C. Kashyap, D. C. Dube; Ceram. Int. 31 (2005) 171-176.
- [14] S. T. Alone, R. H. Kadam, S. E. Shirsath, K. M. Jadhav; Effect of jump lengths of electron and cation distribution study of $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_{2-x}\text{Al}_x\text{O}_4$; Int. J. Moder. Phys. B 25 (2011) 2229.
- [15] E.J. Verwey, J.H. de Boer, Rec. Trans. Chim. Phys. Bas. 55 (1936) 531.
- [16] Urvi V. Chhaya, R.G. Kulkarni, Mater. Lett. 39 (1999) 91-96