Structural and Electrical Properties of Lanthanum Substituted Spinel Ferrites

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Abstract: A series of La-substituted Manganese-Zinc based ferrites of nominal composition $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ for $x = 0.00$- 0.05 in steps of 0.01 was produced by conventional ceramic technique. From X-Ray diffraction patterns, all samples showed single cubic spinel structure as a main phase along with small traces of second phase ($LaFeO_3$). The Lattice constant shows a decreasing trend with the substitution of lanthanum. This may be due to large difference in the ionic radii of Fe^{3+} and La^{3+}ions. La^{3+} ions may not enter into the spinel lattice due to large ionic radius. During the sintering process, some of the La^{3+}ions diffused in to the grain boundaries and can form an insulating ultra thin layer around the grains. This causes the shrinkage of the spinel lattice and hence lattice constant decreases. Dc resistivity and activation energies showed increasing trend with increasing La contents. The temperature dependent resistivity and activation energy decreases with increasing temperature. The structural, physical and electrical properties of La-substituted Manganese-Zinc based ferrites are discussed in the current paper.

Key words: X-ray diffraction $\cdot$ Activation energy $\cdot$ Spinel ferrites $\cdot$ Electrical resistivity $\cdot$ La-Mg-Fe-O

INTRODUCTION

The pure inverse spinel compound $MgFe_2O_4$ has been extensively studied. Magnesium ferrite, $MgFe_2O_4$ is regarded as an important candidate of the spinel family. It has a cubic structure of the normal spinel type and is a soft magnetic n-type semiconducting material, which finds a wide number of applications in heterogeneous catalysis [1], gas sensors [2], transformers, ferrofluids and magnet core of coils [3]. It has been demonstrated that this material can be used for thermal coagulation. Many efforts have been made to improve the basic properties of ferrites by substituting various ions with different valence states. Rare earth substituted magnesium ferrites have attracted considerable attention in the field of technological applications extending from microwave to radio frequency. The rare earth ions are the promising substitute for the improvement of the properties of ferrites. The addition of rare earth metal ions like Gd, La and Tb introduces changes in the structure and texture. [4]. In the fabrication of advanced functional materials, the substitution of small concentrations of different rare-earth

(RE^{3+}) ions in Mn–Zn ferrites has been reported to have marked effects on properties [5]. The most vital requirement is to tune the desirable physical and structural properties of ferrites by means of the substitution of lanthanide ions which induce a change in the size of the spinel lattice due to their larger ionic radii. The formation of compounds with the inverse spinel structure is possible when RE^{3+} substitutes for Fe^{3+} on the octahedral sites, as reported in the case of Ca^{2+} ions in $NiFe_2O_4$ [6]. In the present work La-substituted magnesium zinc ferrites were prepared by a standard ceramic preparation and sintering process. The effect of minor substitutions of La-ions for Fe-ions was studied. The aim of this research was to achieve a comparatively dense ferrite material by lowering the porosity and to investigate the phases developed.

Experimental: The Mg-Zn ferrites having general formula $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ (x=0.00, 0.01, 0.02, 0.03, 0.04, 0.05) were prepared by using convectional ceramic method. The parent oxide materials MgO, ZnO, La_2O_3 and Fe_2O_3 (99.99% pure) were weighed using electronic balance

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having an accuracy up to 10^{-4} grams. These oxide materials were mixed with standard weight percentages, according to their stiochometric calculations using the following equation.

$$0.5MgO + 0.5ZnO + x\ La_2O_3 + (1-x)\ Fe_2O_3 \longrightarrow$$
$$Mg_{0.5}\ Zn_{0.5}\ La_{2x}Fe_{2-2x}\ O_4$$

(1)
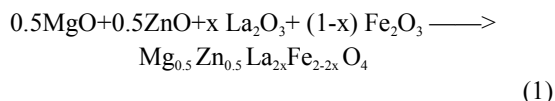
The weighed amount of parent oxide materials were mixed homogeneously in an agate mortar by grinding for four hours. Before and after this process the mortar and pestle were rinsed with acetone. The ground powder was then calcined at 800 C° for 3 hours followed by air quenching. The powder was again ground for fifteen minutes with PVA as binder (4 wt%). This powder was then palletized by using hydraulic pressing machine (PAUL-OTTOWEBER). Each pellet was pressed under the pressure of $30KN/mm^2$. The pellets were pre sintered at 800C° for 03 hours and finally sintered at 1225°C for 06 hours in a box furnace. After final sintering the samples were quenched in air to obtain the equilibrium position of cations on A- and B-sites. Nelson-Relay function was used to calculate the average value of the lattice constant [7]. X-ray density was calculated using the equation, $D_x = 8M/Na^3$ where M is the molecular weight of the sample, 'a' is the lattice constant and 'N' is Avogadro's number. The bulk density "D" is also determined by using Archimedes principles in toluene, using the formula.

$$D = \left(\frac{W_s}{W_t}\right) \times d$$

(2)

where W_s denotes weight of the Specimen in air, W_t is apparent weight loss in toluene and d is density of toluene, with density = 0.867 g/cm^3.Two probe method was used for the d.c. resistivity measurements. A dc power supply and a Keithley multimeter model 197 A was used for measuring current.

RESULTS AND DISCUSSIONS

Representative X-ray diffraction patterns of $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ (x=0.00, 0.01, 0.02, 0.03, 0.04, 0.05) are shown in Fig. (1). Analysis of the XRD patterns confirms the formation of cubic spinel phase as main phase along with few traces of secondary phase. The presence of allowed fcc peaks confirm the formation of cubic spinel structure. A peak corresponding to $2\theta = 32.3$ (indicated by the *) is attributed to secondary phase at the grain boundaries and appears for x ≥ 0.01 and magnitude of intensity increases with the increase of lanthanum concentration. This peak is identified as $LaFeO_3$ (lanthanum iron oxide) matched with ICDDPDF # 39-1489. A possible explanation for the appearance of second phase is that some Y^{3+} ions diffused to the grain boundaries and react with Fe to form second phase $YFeO_3$ [8].

Fig (2) shows the lattice constant vs La concentration for $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ system. An appreciable decrease of the lattice parameter was observed for La-substituted Mg-Zn ferrites. The decrease in the lattice constant may be attributed to the large difference of ionic radius of La^{3+} (1.17A°) and other cations, Mg^{1+}(0.65 A°) Fe^{3+}(0.78A°) Zn^{2+}(0.74 A°). Due to large ionic radii La^{3+} ions may not
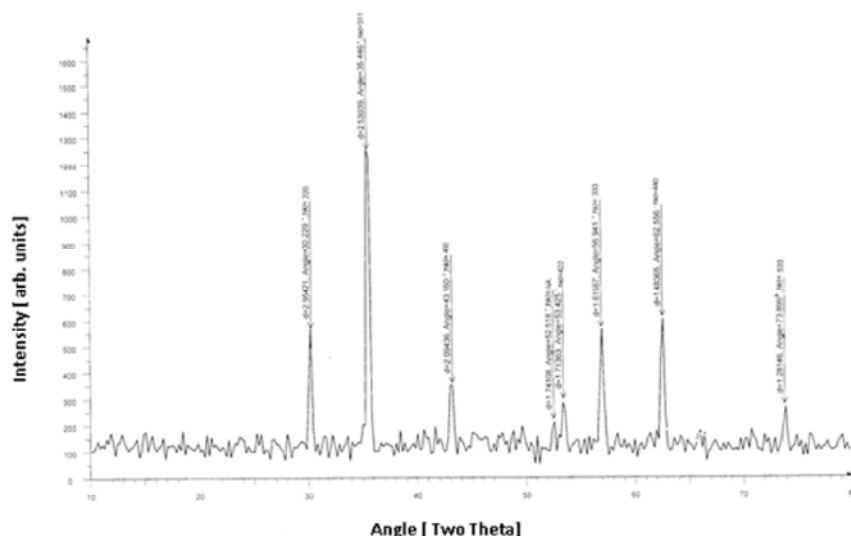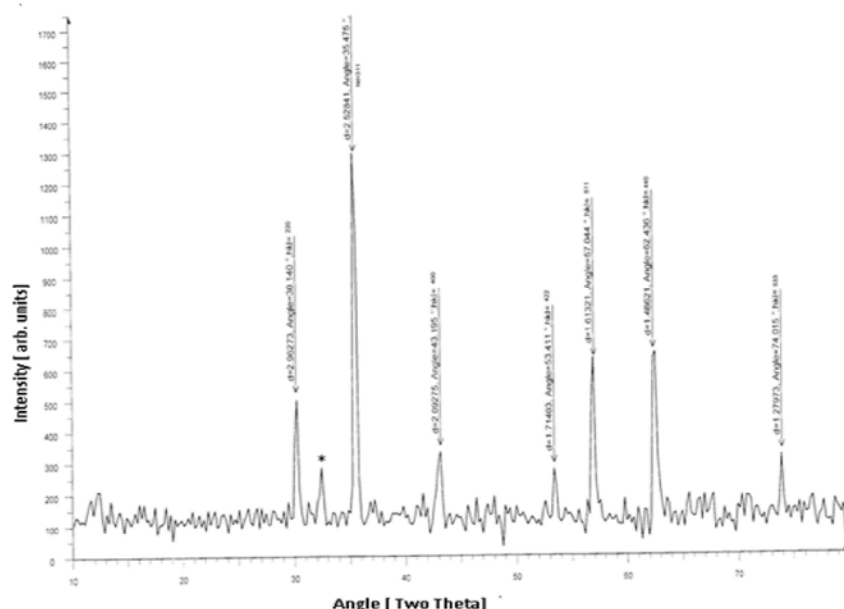

Fig. 1(a): XRD pattern for $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ for ferrites (x = 0.00)

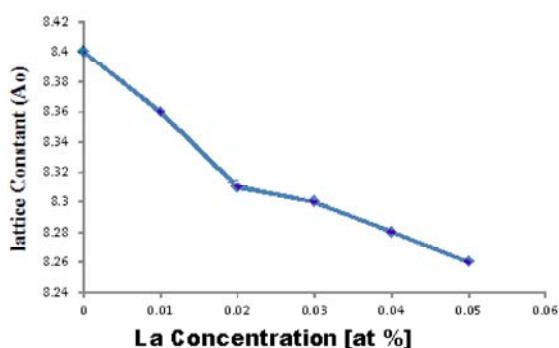Fig. 1(b): XRD pattern for $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ for ferrites (x = 0.02)

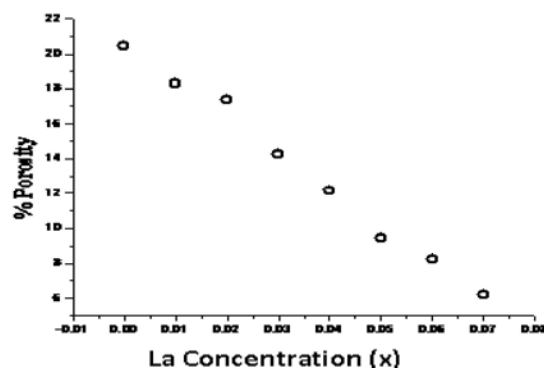Fig. 2: Lattice Constant (A^0) Vs La-Concentration (x) for $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ ferrites ($0 \le x \le 0.05$)

Fig. 4: % porosity Vs La-Concentration (x) for $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ ferrites ($0 \le x \le 0.05$)
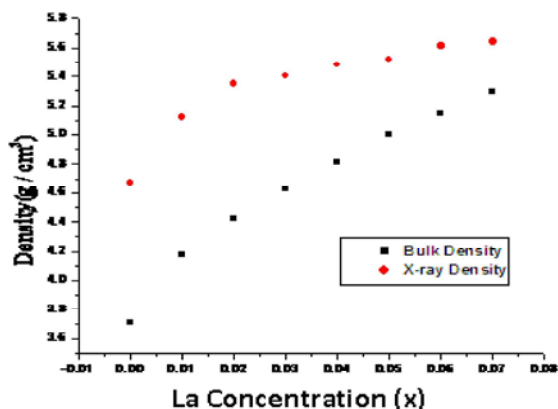

Fig. 3: Bulk density and X-ray density Vs La-concentration(x) for $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ ferrites ($0 \le x \le 0.05$)

enter in to the spinel lattice. During the sintering process, some of the La^{3+}ions diffused in to the grain boundaries and can form an insulating ultra thin layer around the grains. This causes the shrinkage of the spinel lattice and hence lattice constant decreases [9]. Fig (3) shows the bulk density (D_s) and X-ray density (D_x) Vs La-concentration. It can be observed that bulk densities are smaller in magnitude than corresponding X-ray densities. The large value of X-ray density (D_x) than bulk density (D_s) may be due to existence of pores [10]. The porosity (%) is calculated by using the following relation, is depicted in Fig. (4).

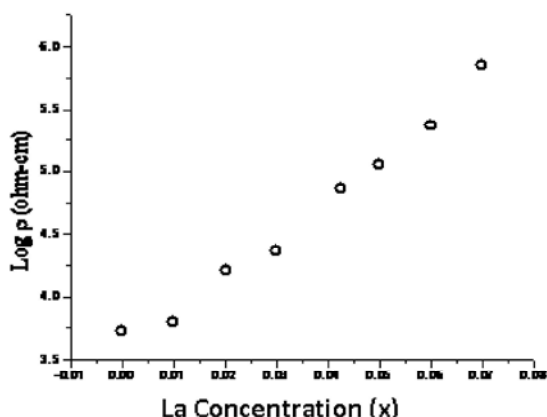$$P = \left(1 - \frac{D_s}{D_x}\right) \times 100 \qquad (3)$$

Fig. 5: Room temperature resistivity Vs La-Concentration (x) for $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ ferrites ($0 \leq x \leq 0.05$)

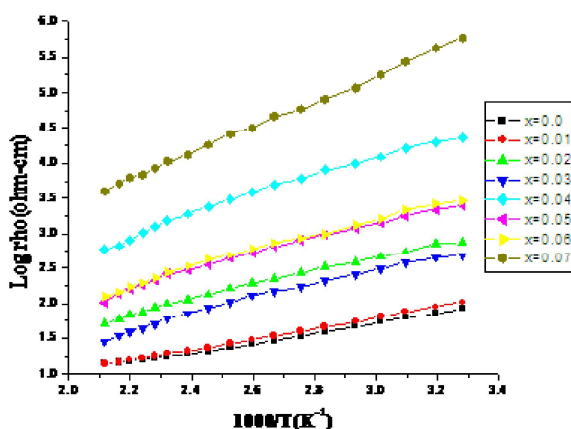Fig. 6: Plot of Logρ Vs 1000/T for $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ ferrites ($0 \leq x \leq 0.05$)
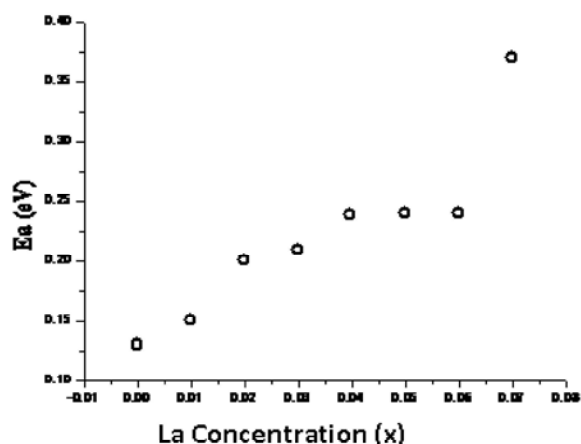

Fig. 7: Activation energy (ev) Vs La-Concentration (x) for $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ ferrites ($0 \leq x \leq 0.05$)

It is known that the porosity of ceramic samples results from two sources, interagranular porosity and intergranular porosity. The intergranular porosity mainly depends on the grain size. At high sintering temperatures the density is decreased because intragranular porosity increases resulting from discontinuous grain growth [11]. There is lowering of porosity from about 20% to 6% by incorporation of Lanthanum. The reason of porosity lowering is that the Lanthanum ion which enters in to the lattice partially, during the sintering process, will diffuse to the grain boundaries and form an ultra thin layer around the grains. This segregation process impedes (lessen) the displacement of grain boundaries and further crystal growth is stemmed. This results in quite smaller grains, with a reduced number of inner pores [12]. It is well known that the electrical conductivity in solids is highly sensitive to variations in stoichometry and defect formation [13]. Room Temperature dc resistivity of $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ (x=0.00, 0.01, 0.02, 0.03, 0.04, 0.05) vs La concentration shows a drastic increase from 5.3 $\times$ 10^3 to 7.1×10^5 Ω-cm to a maximum value at x = 0.05, as shown in Fig (3). Relecu *et al.* reported high resistivity for the RE substituted ferrites with large ionic radii. On the other hand, the formation of insulating intergranular layers impedes the oxidation of Fe^{2+} ions inside the grains during the slow cooling of the samples and on the other hand, it increases the resistivity of the material [14]. The increase in resistivity may also be attributed to the increase of the intragranular porosity which in turn hinders the motion of the charge carriers [15]. Temperature dependent dc electrical resistivity of $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ system has been measured in temperature range (30 - 200°C) as shown in Fig (7). Each sample follows the Arrhenius equation, which predicts the semi-conducting nature of the samples. The plots show that the resistivity (ρ) decreases as the temperature increases which indicates semi-conductor behavior of the samples [10]. The steeper slope of (log ρ vs 1/T) for all the samples of $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ can be regarded as due to thermally activated mobility of charge carriers, but not to a thermally activated creation of these carriers. It can be observed that all the samples are degenerate type semi conductors. The activation energy obtained from Arrhenius plots increases with the increase of La substitution as shown in Fig (4). It can also be concluded that samples having low resistivity have low activation energy and vice versa [15] as predicted by Fig. (3) and (4). Activation energy is larger for La-substituted samples than un-substituted one. This result suggests the existence of conduction sensitive to structure [16].

CONCLUSION

Structure and electric properties of different composition prepared by standard ceramic method has been investigated and results discussed systematically. X-ray diffraction analysis reveals that $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ for x = 0.00 ---- 0.05 in steps of 0.01 samples clearly indicate formation of cubic spinel crystal structure and secondary phase is also identified in last four samples. Lattice constant exhibits decrease as a function of La concentration (X). Room temperature dc resistivity of $Mg_{0.5}Zn_{0.5}La_{2x}Fe_{2-2x}O_4$ ferrites increases with lanthanum concentration (X). This was attributed to the formation of insulating intergranular layers that impedes the oxidation of Fe^{2+} ions inside the grains. Temperature dependent dc electrical resistivity decreases as the temperature increases which is indicating semi-conductor behavior of the samples. It was concluded that samples having low resistivity have low activation energy and vice versa. High value of dc resistivity makes this ferrite suitable for the high frequency applications where eddy current losses become appreciable.

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