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Cation Distribution of $Mg_{0.6}Zn_{0.4}La_{2y}Fe_{2-2y}O_4$Spinel Ferrite Nanocomposites

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Abstract: Nanocompositesof Lanthanum substituted Magnesium Zinc ferrites with general formula $Mg_{0.6}Zn_{0.4}La_{2y}Fe_{2-2y}O_4$(where y = 0.0, 0.05, 0.1, 0.15, 0.20 and 0.25) have been synthesized using co-precipitation method. Phase formation was investigated using X-ray diffraction (XRD) technique and confirms cubic spinel structure. Effect of lanthanum substitution on structural and cation distribution was studied using X-ray diffraction technique.

Keywords: *La^{3+} substituted magnesium zinc ferrites, Cation Distribution*

1. Introduction

Nano-sized polycrystalline ferrite is of technological and scientific interesting as compare to bulk materials due to it's significantly differ from those of physical, chemical, optical, electrical and magnetic properties [1-3]. Nanosized spinel ferrites possess high electrical resistivity, low eddy current losses, low dielectric losses, high Curie temperature, moderate saturation magnetization, high permeability etc. Today these significant properties make ferrite useful in wide range of application in electronics and telecommunications [4] hyperthermia [5], sensors [6], inductors and RF ICs [7], gas Sensors [8], ferro-fluids [9], drug delivery and spintronics. The Mg-Zn ferrites are one of the most promising materials used in microwave frequency application due to their high resistivity and low dielectric losses, while used in storage device due to low saturation magnetization and chemical stability. The most popular combinations Mg-Zn are substituted with rare earth element associated with excellent properties. In present investigation, we report effect of La content on cation distribution of Mg-Zn ferrite.

2. Experimental

The $Mg_{0.6}Zn_{0.4}La_{2y}Fe_{2-2y}O_4$ (where y = 0.00, 0.05, 0.10, 0.15, 0.20 & 0.25) have been synthesized by co-precipitation method as per reported literature protocol [10]. The analytical reagent grade precursors $MgSO_4.7H_2O$, $ZnSO_4.7H_2O$, $LaSO_4.7H_2O$ and $Fe_2SO_4.7H_2O$ were purchased from spectrochem India Ltd. and used as received. The powdered product of co-precipitation obtained was calcined at 450^{o}C for 5 h and then pre-sintered at 700^{o}C for 5 h in air medium. Lastly, the prepared pellets were sintered at 900^{o}C for 12 h in air.

3 Result and discussion

The XRD patterns of $Mg_{0.6}Zn_{0.4}La_{2y}Fe_{2-2y}O_4$ (where, y=0.00, 0.05, 0.10, 0.15, 0.20 and 0.25) ferrite system sintered at temperature 900^{o}C for 12h are revealed in Fig.1.

The XRD pattern reveals the intense and sharp peaks matching to the planes (220), (311), (222), (400), (422), (511), (440), (620) and (533). The peaks obtained in the diffractogram closely match the data in the JCPDS file card number (04-002-5442). The XRD peak pattern corresponds to all allowed planes, which hint outs single phase structure furthermore the trace of secondary phase for La^{3+} substituted Mg-Zn ferries [11] and for Ni-Zn-Cr ferrites [12].Moreover, the peak at $2\theta = 32.10^\circ$ corresponds to plane (121) which is recognized to secondary phase for $LaFeO_3$ indexed as per ICDD file No. 01-74-9045.

With increase in La content, intensity of characteristics peak for Fe_2O_4 gradually decreases, while intensity of peak (121) of $LaFeO_3$ increases. It implies that during auto-combustion reaction at the time of sintering, heat is released, which is insufficient for the formation of single phase ferrite. This result into La^{3+} ion not getting substituted in the lattice properly for the reason of the higher bond energy of $La^{3+} - O^{2-}$ with respect to bond

energy of $Fe^{3+} - O^{2-}$. The extra energy is required to form La^{3+} ions pierce into lattice and create the bond of $La^{3+} - O^{2-}$. Consequently, thermal stability of lanthanum substituted ferrite was higher as compare to pure ferrite and additional energy is required for the formation of La-substituted ferrites [13]. Subsequently, the substituted La^{3+} ions have a limit of solubility within the spinel lattice. The degree of substitution of Fe^{3+} by La^{3+} ion depends upon ionic radii. Forever, a few La^{3+} ions not pass into the spinel lattice and react with Fe^{3+} ions resulting in formation of secondary phase of ortho ferrite $LaFeO_3$ reside at grain boundaries. If a La^{3+} ions exactly enters into octahedral site then the number of Fe^{3+} ions on octahedral site strongly distorted [13]. Similar observation have been reported in lanthanum substituted nickel [14], Cadmium [15] and Ni-Zi ferrites [16, 17].

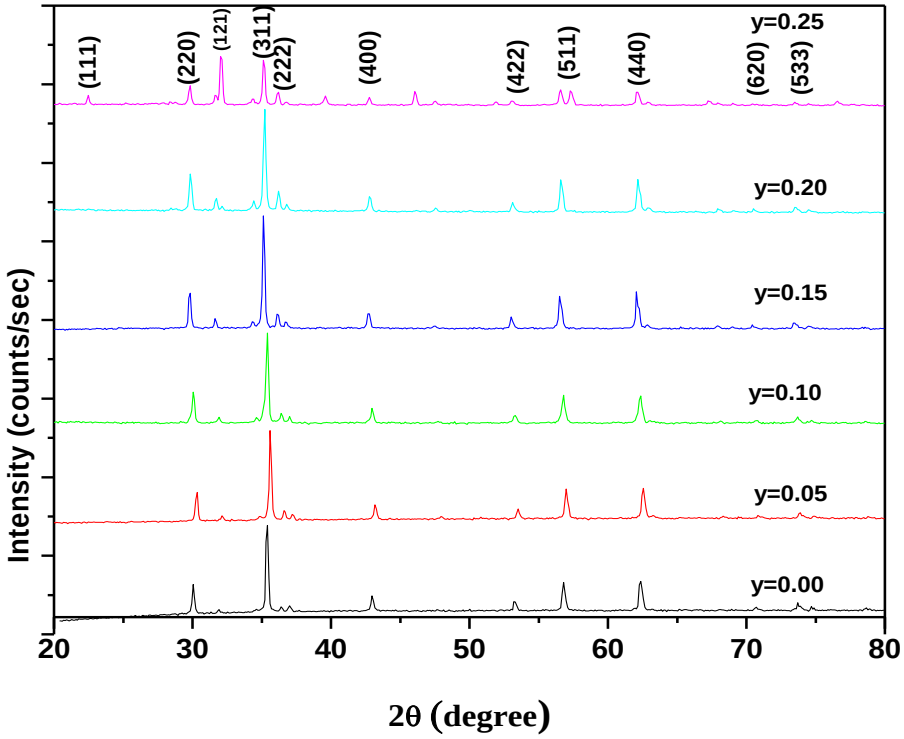

Fig.1: XRD patterns of $Mg_{0.6}Zn_{0.4}La_{2y}Fe_{2-2y}O_4$ferrites.

In present work, cationic distribution of $Mg_{0.6}Zn_{0.4}La_{2y}Fe_{2-2y}O_4$ (where, y = 0.00, 0.05, 0.10, 0.15, 0.20 and 0.25) ferrite were estimated by x-ray data. The intensity of line was computed by using the relation (1) given by Buerger[18].

$$I_{hkl} = |F_{hkl}|^2 . P . L_p \quad \text{---------- (1)}$$

Where, I_{hkl} =relative intensity

F_{hkl} =structure factor

P = multiplicity factor

L_pLorentz polarization factor

The intensities of (220) and (422) planes are mostly effective to cations on the tetrahedral sites [19].while the intensities of (400) plane depends on ions on both the sites [20,21]. The intensities of reflections plane (220), (400), (422) and (440) were determined by computer running program of calculation of x-ray diffraction intensity for spinel structure. The observed and calculated values of intensity ratios of I(220) / I(440), I(422)/I(440) and I(440) / I(400) were evaluated for all the possible cationic distribution at A and B site as described in [22] and shown in table1.Table 2 illustrates the occupation of cations Mg^{2+}, Zn^{2+}, Fe^{3+} and La^{3+} ions on Aand B site.

Table 1: Observed and calculated intensity ratio of (220), (400), (422) and (440) planes.

La^{3+} content 'y'	$\left(\frac{I_{220}}{I_{440}}\right)_{obs}$	$\left(\frac{I_{220}}{I_{440}}\right)_{Cal}$	$\left(\frac{I_{422}}{I_{440}}\right)_{obs}$	$\left(\frac{I_{422}}{I_{440}}\right)_{Cal}$	$\left(\frac{I_{440}}{I_{400}}\right)_{obs}$	$\left(\frac{I_{440}}{I_{400}}\right)_{Cal}$
0.00	0.9472	0.9123	0.7578	07365	1.2502	1.1154
0.05	0.9522	0.9254	0.7442	0.7235	1.2504	1.2111
0.10	0.9415	1.0127	0.7448	0.7923	1.2650	1.3676
0.15	0.9356	0.8934	0.7658	0.7345	1.2475	1.1981
0.20	0.9613	0.9367	0.7446	0.7122	1.2531	1.1981
0.25	1.01312	1.3264	0.7504	0.7287	1.2258	1.3543

In Mg-Zn ferrite, it was found that Zn^{2+} ion have strong tendancy to occupy at A-site. However, Mg^{2+} ion have strong preference to occupy at B-site and are present on both A and B site. The Fe^{3+} ions are statistically distributed among A-site and B-site in spinel lattice. Upon the addition of lanthanum in Mg-Zn ferrite, it was found that, La^{3+} replaces the Fe^{3+}ions at B-sites, while a some Mg^{2+} and Zn^{2+} ions are move from A-site to B-site and some Fe^{3+} ions move from the B-site to A-site

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Table 2: Cation distribution for $Mg_{0.6}Zn_{0.4}La_{2y}Fe_{2-2y}O_4$ferrites

La^{3+} content y	A-Site	B-Site
0.00	$Mg^{2+}_{0.15}Zn^{2+}_{0.35}Fe^{3+}_{0.5}$	$Mg^{2+}_{0.45}Zn^{2+}_{0.05}Fe^{3+}_{1.15}Fe^{2+}_{0.35}La^{3+}_{0.0}$
0.05	$Mg^{2+}_{0.13}Zn^{2+}_{0.31}Fe^{3+}_{0.56}$	$Mg^{2+}_{0.47}Zn^{2+}_{0.09}Fe^{3+}_{1.04}Fe^{2+}_{0.30}La^{3+}_{0.1}$
0.10	$Mg^{2+}_{0.11}Zn^{2+}_{0.27}Fe^{3+}_{0.62}$	$Mg^{2+}_{0.49}Zn^{2+}_{0.13}Fe^{3+}_{0.93}Fe^{2+}_{0.25}La^{3+}_{0.2}$
0.15	$Mg^{2+}_{0.09}Zn^{2+}_{0.23}Fe^{3+}_{0.68}$	$Mg^{2+}_{0.51}Zn^{2+}_{0.17}Fe^{3+}_{0.82}Fe^{2+}_{0.20}La^{3+}_{0.3}$
0.20	$Mg^{2+}_{0.07}Zn^{2+}_{0.19}Fe^{3+}_{0.74}$	$Mg^{2+}_{0.53}Zn^{2+}_{0.21}Fe^{3+}_{0.71}Fe^{2+}_{0.15}La^{3+}_{0.4}$
0.25	$Mg^{2+}_{0.05}Zn^{2+}_{0.15}Fe^{3+}_{0.80}$	$Mg^{2+}_{0.55}Zn^{2+}_{0.25}Fe^{3+}_{0.60}Fe^{2+}_{0.10}La^{3+}_{0.5}$

4. Conclusion

In conclusion, we report the Cation distribution of lanthanum substituted magnesium zinc ferrites by co-precipitation method. Lanthanum substituted magnesium zinc ferrite is cubic spinel ferrite. Upon the addition of lanthanum in Mg-Zn ferrite, it was found that, La^{3+} replaces the Fe^{3+}ions at B-sites, while a some Mg^{2+} and Zn^{2+} ions are move from A-site to B-site and some Fe^{3+} ions move from the B-site to A-site.

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