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Magnetic properties of LiZnCu ferrite synthesized by the microwave sintering method

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ABSTRACT

Lithium ferrites have attracted considerable attention because they have been used as replacements for garnets due to their low cost. A series of polycrystalline ferrite samples were prepared with the composition of $Li_XZn_{(0.6-2X)}Cu_{0.4}Fe_2O_4$($X$=0.05, 0.1, 0.15, 0.2, 0.25, 0.3) at chemical reaction temperature 150 °C by sintering with microwave assisted combustion method. The characterization shows the formation of single phase cubic structure when carried out by using the X-rays technique and *I–R* technique. Magnetization parameters such as saturation magnetization, coercivity, magnetic moment were calculated by using the Hysteresis graph. The Curie temperature obtained using the susceptibility data are found to be in the range 350–700 °C. Anhysteric remanent magnetization is used for estimating the grain size and domain structure of the composition. An attempt has been made to synthesis the nano-particles at lower reaction temperature by using non-conventional microwave sintering method. The advantage of this method is its lower sintering temperature and time compared to the conventional ceramic technique and direct formation of nano-ferrites without ball-milling.

1. Introduction

Lithium ferrite has been a widely investigated material due to its importance in construction and engineering of many electromagnetic and microwave devices. Lithium ferrite is an inverse spinel compound has interesting magnetic properties when it is doped with magnetic or diamagnetic impurities. Li ferrite is an attractive and important material for microwave application [1–3]. Lithium and substituted lithium ferrites is found to be an excellent material in high density recording media, absorbers and microwave devices due to their low cost, high saturation magnetization, high Curie temperature and hysteresis loop properties, that offer advantageous performance over other spinel structure [4]. Doping of a small amount of the divalent metallic ions or rare earth ions in spinel ferrites may modify their electromagnetic properties, which would also lead to modification in their microwave absorbing properties. Therefore in the present work, we have focused on the effects of Zn substitution and the chemical reaction temperature on the magnetic properties of Li–Cu ferrites synthesized by microwave sintering method. The present work is focused on a combination of lower chemical reaction temperature followed by microwave sintering for the completion of solid state reaction that could be useful for obtaining nanoferrites.

2. Experimental

2.1. Synthesis

Ferrites having the general formula $Li_XZn_{(0.6-2X)}Cu_{0.4}Fe_2O_4$ (X=0.05, 0.1, 0.15, 0.2, 0.25, 0.3) have been prepared at the chemical reaction temperature 150 °C and sintered using non-conventional microwave sintering method. AR-grade ferric nitrate, zinc nitrate, copper nitrates, lithium nitrate were used as the starting material. The stoichiometric proportions of the nitrates were weighed and added in 100 ml of distilled water to produce an aqueous solution. The solution was kept in paraffin oil bath at

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chemical reaction temperature 150 °C. It was continuously stirred with the magnetic stirrer for three hours. As a result the fumes of nitrates released were converted into thick slurry. The slurry was then transformed into the modified microwave oven (Model-GMS 17M07 WHGX). The microwave assisted synthesis carried out in modified domestic microwave oven operating at maximum power output of 700 W. The irradiation was given in the form of pulses for duration of 1 min for nearly 30–32 min and the process was stopped when nitrous gases got evaporated completely. Finally the required brown colored composition was formed. The obtained ferrite powder was then crushed in agate mortar.

2.2. Characterizations

The completion of solid state reaction was confirmed by X-ray diffraction patterns taken on powder samples using a by X-ray Diffractometer D 8 Advance (by M/s Bruker AXS), GmbH, Germany, using Cukα ($\lambda = 1.540589$ Å) radiation. Saturation magnetization measurements were carried out using a MicroMag 2900-Alternating Gradient Magnetometer (AGM) (Princeton Measurements Corporation). AC susceptibility of powdered samples was measured in the temperature range 400–800 °C on a AGICO KLY-45 KappaPridge set up. The scanning electron micrographs were taken using an SEM instrument JSM-7600 F (Magnification × 25–1,000,000).ARM measurements were taken by using demagnetization of the sample using a demagnetizer D-2000AF (ASC Scientific).

3. Results and discussions

3.1. Structural characteristic

The single phase spinel structure of the prepared ferrite samples was confirmed from XRD pattern. A typical XRD pattern for $Li_XZn_{(0.6-2X)}Cu_{0.4}Fe_2O_4$ ($X = 0.05, 0.1, 0.15, 0.2, 0.25, 0.3$) ferrite samples is shown in Fig. 1. Lattice parameter shows variations with the reaction temperature and Zinc concentration. The obtained values of lattice parameter are in the range 8.3690 A° to 8.4653 A°. The bondlengths linearly increases with Zn^{2+} content. The increase in bondlength can be attributed to the increase in lattice parameter 'a' with Zn content.

3.2. Saturation magnetization (M_s)

The hysteresis curves for the $Li_XZn_{(0.6-2X)}Cu_{0.4}Fe_2O_4$ recorded at room temperature is shown in Fig. 2. From the curve, saturation magnetization and coercivity values were calculated and are listed in Table 1. Saturation Magnetization M_s and magnetic moment ranging from 13.71 emu/gm to 36.19 emu/gm and 0.6 μB to 1.5 μB. These parameters depend on the microstructure and distribution of cations on the A and B sites of the spinal structure. It is seen that the saturation magnetization M_s values and magnetic moment are found to increase with the increase in Zn concentration for $X \geq 0.2$, obeying Neel's model for magnetization and decreases thereafter for $X = 0.15$ & 0.1 suggests the existence of non-collinear spin interaction [4,5]. For higher concentration of Zn ($X = 0.05$), the sample shows the increase in saturation magnetization and magnetic moment. This is due to the dilution of magnetization of the A-sublattice by non-magnetic Zn^{2+} ions, which can be explained on the basis of Neel's two sublattice models [6]. The total magnetization of the spinel ferrites comes from the difference in the magnetization of B and A site and it is also known that the octahedral site has larger magnetic moment than the tetrahedral A site. When the Zn^{2+} ions replace the Fe^{3+} ions at A site, the Fe^{3+} ions migrate to B site and this increases the saturation magnetization. The Fe^{3+} ions have larger magnetic moment than Cu^{2+}, Zn^{2+} and Li^{2+} ions. With further increase in Zn^{2+} ions, the magnetic moment on the B site increase and it increases the B–B exchange interaction induces anti parallel spin coupling that decreases the magnetization. The obtained values of saturation Magnetization and coercivity are less as compared to the other reported values [7,8]. This is attributed to the effect of chemical reaction temperature and the method of preparation. Magnetic properties are structure dependent while structure properties depend on the preparation technique.

3.3. Coercivity (H_c)

The coercivity H_c of the formed LiZnCu ferrite is listed in Table 1. It is seen that the coercivity decreases with increase in Zn^{2+} concentration and at higher values of Zn^{2+} concentration coercivity increases. The decrease may be related to the microstructure of the sample [9]. The coercivity is inversely proportional to the grain size.

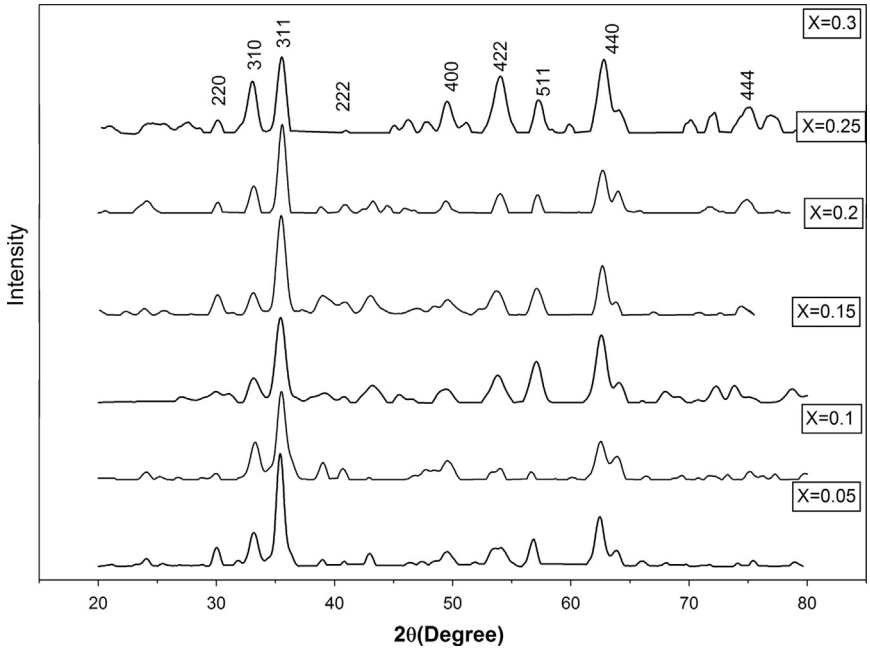

Fig. 1. XRD for the $Li_XZn_{(0.6-2X)}Cu_{0.4}Fe_2O_4$ ($X = 0.05, 0.1, 0.15, 0.2, 0.25, 0.3$) ferrite.

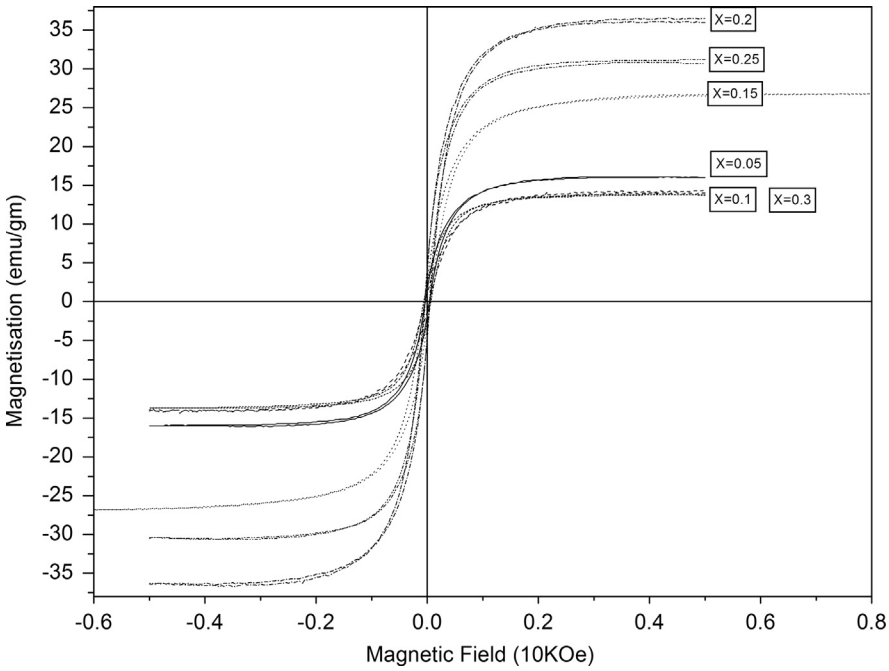

Fig. 2. Hystersis loop for the composition for $Li_XZn_{(0.6-2X)}$ $Cu_{0.4}Fe_2O_4$ (X=0.05,0.1, 0.15, 0.2, 0.25,0.3) ferrite.

Table 1
Saturation magnetization, magnetic moment, coercivity, Curie temperature and ARM of $Li_XZn_{(0.6-2X)}Cu_{0.4}Fe_2O_4$ (X=0.05, 0.1, 0.15, 0.2, 0.25, 0.3) ferrite.

Composition X	Saturation magnetizat-ion (emu/gm)	Magnetic moment (μB)	Coercivity (Oe)	Curie temperature (° C)	Mass specific Susceptiblity χ	ARM (emu/gm)	ARM/χ_{mass} (Oe)
0.05	16	0.7	36.38	405	0.38424	892.3	18.4×10^4
0.1	14.02	0.63	36.57	400	0.144319	340	18.7×10^4
0.15	26.78	1.15	52.69	475	0.269358	1155.08	34.1×10^4
0.2	36.19	1.5	49.98	520	0.359681	1369.88	30.3×10^4
0.25	30.79	1.3	38.48	554	0.265103	1429.69	42.9×10^4
0.3	13.71	0.6	63.62	600	0.150307	1074	56.8×10^4

A larger grain size makes the motion of the domain walls easier and thereby the coercivity decreases. With increase in Zn^{2+} content, redundant Zn^{2+} ions may reside at the grain boundaries and form secondary phase. The presence of secondary phase at the grain boundaries may not only inhibit the motion of the magnetic domain walls but may also induce some distortion within the grains leading to the initiation of the internal stress. The coercivity is influenced by the factors such as magnetocrystallinity, micro-strain, magnetic particle morphology and size distribution, anisotropy and magnetic domain size [9].

3.4. AC susceptibility and Curie temperature

The measurement of magnetic susceptibility is very useful technique to obtain much important information regarding physical, chemical and magnetic states of the substance. The ratio of induced magnetization to the applied field is known as the magnetic susceptibility. The mass specific susceptibility of the composition is listed in Table 1. Mass specific susceptibility shows the same variation as the saturation magnetization.

The thermal variation of low field AC susceptibility gives information regarding transition temperature, type of magnetic ordering of the substance. The variation of normalized A.C susceptibility with temperature is shown in Fig. 3. It is seen that for the samples with the X=0.05 and X=0.1, susceptibility decreases with increase in temperature. This indicates the presence of superparamagnetic structure. Whereas for the sample with X=0.15 and X=0.2, A.C susceptibility has been found independent of temperature and drops off at Curie temperature, which suggests the existence of Multidomain structure [10].The composition X=0.25, and 0.3, χ_{AC} increases slowly and shows a peak at blocking temperature and then decreases sharply to zero at Curie point. The sharp decrease in χ_{AC} confirms the strong homogeneity of the sample. This suggests the sample exhibit single domain structure [11]. Thus the substitution of Zn^{2+} ions to $LiCuFe_2O_4$ alters the domain structure from SD to MD and then to SP. Change in domain structure was observed.

Curie temperature is the temperature at which susceptibility drops off sharply in normalized susceptibility curve. The Curie temperature is the measure of relatively weighted magnetic interaction per formula unit. Stronger the magnetic interaction larger will be the Curie temperature. The Curie temperatures are listed in Table 1. The variation of Curie temperature with Zn concentration is shown in Fig. 4. The range of Curie temperature is 400–600 °C. It is seen that the Curie temperature decreases with increase in Zn^{2+} content. The Curie temperature mainly related to the strength of A–B interaction. The substitution of Zn^{2+} should decrease the strength of A–B interaction which consequently requires less thermal energy to offset the spin alignment and Curie temperature decrease. The non-magnetic Zn^{2+} ion reduces the magnetization. When doping of Zn^{2+} increases, the number of magnetic ions on A site is comparatively lower which reduces the magnetic moment of A site, therefore A–B interaction weaken resulting in lower Curie temperature.

In the present communication the sample shows SP, SD and MD structure whose chemical reaction carried out at lower temperature

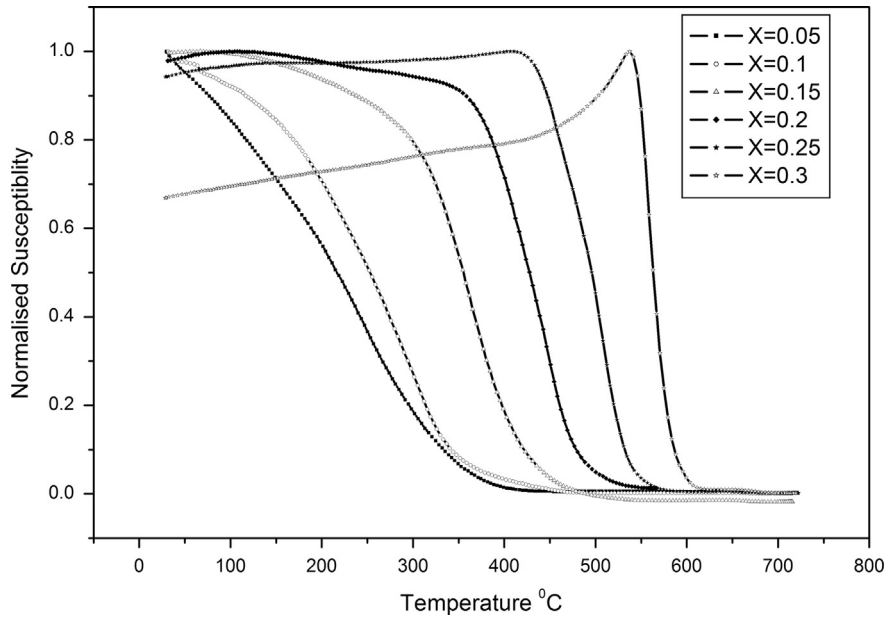

Fig. 3. Normalized susceptibility for the composition prepared at 150 °C for $Li_XZn_{(0.6-2X)}Cu_{0.4}Fe_2O_4$ (X=0.05,0.1, 0.15, 0.2, 0.25,0.3) ferrite.

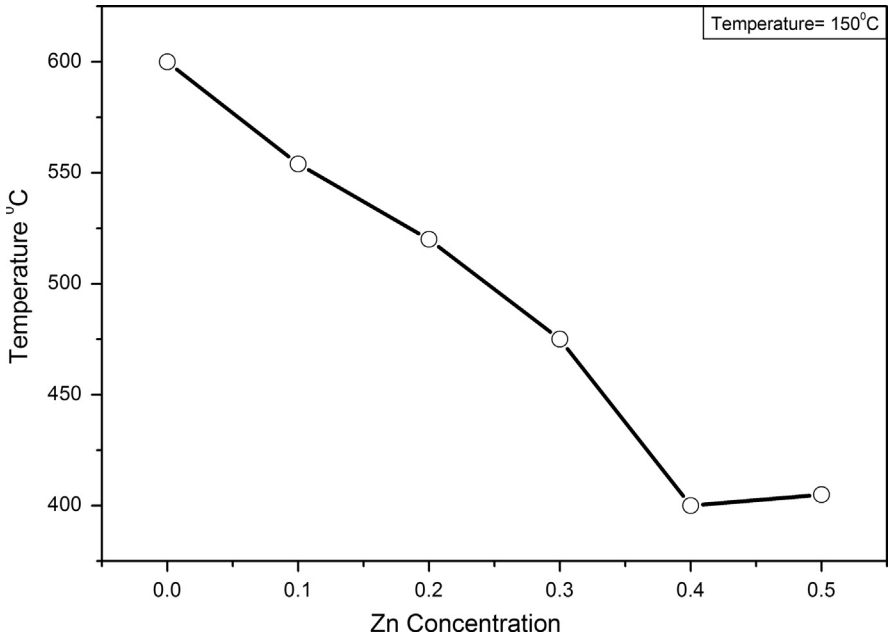

Fig. 4. Variation of curie temperature with Zn concentration for $Li_XZn_{(0.6-2X)}Cu_{0.4}Fe_2O_4$ (X=0.05,0.1, 0.15, 0.2, 0.25, 03).

as compared to other reported value [11,12]. Rendale et al. ([13]) have reported the SP and single domain structure for LiZnMg ferrites synthesized using the sucrose precursor method and sintered at 800 °C for 8 h.

3.5. Morphology of the sample

Magnetic and electrical properties sensitively depend on the microstructure of ferrite. Fig. 5 shows the microstructure of the sample X=0.2. It indicates that the ferrite particles obtained by this method having agglomeration to some extent due to the relative microwave sintering and interaction between magnetic particles. The particle sizes of the samples prepared at 150 °C are in the range 43–63 nm. It can be found from Fig. 5 that the particle size of Zn substituted ferrites are increases with increase in Zn concentration and the particles are in slightly agglomerated state which may be beneficial towards having good packing density of the material leading to higher bulk capacity [14].

3.6. Anhysteretic remanent magnetization-

Various magnetic parameters are commonly used for estimating the grain size of magnetic particles. Microstructure of the composition is shown in Fig. 5. ARM in fine particles is the key to understand the magnetic interactions. Study of ARM in fine particles have been made because of its importance in the recording process on magnetic tapes [15].

ARM is measured by subjecting a sample to an increasing, then decreasing alternating field in the presence of a weak DC bias field. ARM is used to characterize magnetic carriers and to determine domain state. ARM allows estimation of concentration and presence of finer ferromagnetic materials. SSD particles have high

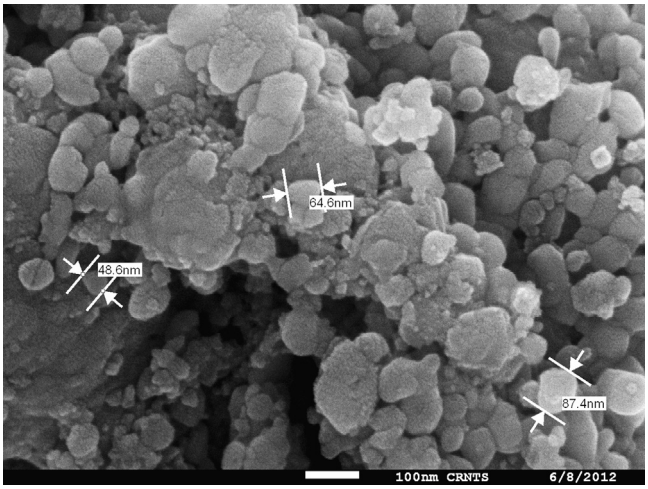

Fig. 5. SEM for the composition for $X=0.2$ prepared at 150 °C.

ARM intensities per unit mass compared to MD particles. Obtained ARM values are in the range 340–1429.69 emu/gm. In magnetite the ARM shows the dependence with grain size. ARM/χ_{mass} values are calculated to find the stability of the magnetic particle and those are in the range of 18.47×10^4–56.85×10^4 Oe.

4. Conclusions

A combination of lower chemical reaction temperature for molecular level mixing followed by microwave sintering could be useful for obtaining nano-ferrites with required parameters.

The X-ray diffraction patterns have confirmed the formation of single phase spinel cubic structure.

The saturation magnetization and Curie temperature shows dependence with Zn concentration. The reaction temperature can be exploited for the production of fine magnetic powder of various sizes.

ARM is used to characterize magnetic carriers and determines domain state and grain size.

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References

[1] P.D. Baba, G.M. Argentina, W.E. Courtney, G.F. Dionne, D.H Timme, Fabrication and properties of microwave lithium ferrites, IEEE Trans. Magn. MAG_8 (1) (1972) 83–94.

[2] M. George, S.S. Nair, A.M. John, P.A. Joy, M.R. Anantharaman, Structural, magnetic and electric properties of the sol–gel prepared $Li_{0.5}Fe_{2.5}O_4$ fine particles, J. Phys. D: Appl. Phys. 39 (2006) 900–910.

[3] G.F. Dionne, Properties of ferrites at low temperatures (invited), J. Appl. Phys. 81 (1997) 5064–5069.

[4] B.P. Ladgaonkar, C.B. Kolekar, A.S. Vaingankar, Infrared absorption spectroscopic study of Nd^{3+} substituted Zn–Mg ferrite, Bull. Mater. Sci. 25 (2002) 351–354.

[5] B.P. Ladgaonkar, P.N. Vasambekar, A.S. Vaingankar, Effect of Zn^{2+} and Nd^{3+} substitution on magnetization and AC susceptibility of Mg ferrite, J. Magn. Magn. Mater.210 (2000) 289–294. http://dx.doi.org/10.1016/S0304-8853(99)00468-0.

[6] S.S. Bellad, R.B. Pujar, B.K. Chougule, Structural and magnetic properties of some mixed Li–Cd ferrite, materials, Chem. Phys. 52 (1998) 166–169. http://dx.doi.org/10.1016/S0254-0584(98)80019-9.

[7] P. Vijaya Bhaskar Reddy, V.R. Reddy, A. Gupta, R. Gopalan, Ch. Gopal Reddy, Mossbauer study of nanocrystalline Li–Zn ferrites, Hyperfine Interac. 183 (2008) 81–86.

[8] S.A. Jadhav, Magnetic properties of Zn substituted Li–Cu ferrites, J. Magn. Magn. Mater. 224 (2001) 167–172.

[9] Jiang Jing, Li Liangechao, Xu Feng, Structural analysis and Magnetic properties of Gd doped Li–Ni Ferrites prepared using Rheological phase reaction method, J. Rare Earth25 (2007) 79–83.

[10] A.Y. Lipare, P.N. Vasambekar, A.S Vaingankar, A.C susceptibility study of $CaCl_2$ doped copper zinc ferrite system, Bull. Mater. Sci. 26 (5) (2003) 493–497.

[11] P.N. Vasambekar, C.B. Kolekar, A.S. Vaingankar, Cation distribution and susceptibility study of Cd–Co and Cr^{3+} substituted Cd–Co ferrites,, J. Magn. Magn. Mater. 186 (1998) 333–341.

[12] M. Raza Ahmad Yasir Jamil, Abdul HafeezHaq Zia ulAmin Nasir, Microwave assisted synthesis of fine magnetic manganese ferrites using the co-precipitation technique, Pak, J. Agric. Sci. 45 (3) (2008) 59–64.

[13] M.K Rendale, S.D. Kulkarni, Vijaya Puri, Magnetic properties of $Li_XMg_{0.7-2X}Zn_{0.3}Fe_{2+X}O_4$ synthesized using sucrose precursor, Arch. Appl. Sci. Res. 3 (5) (2011) 491–497.

[14] Anjan Sir Priti Singh, Mala Nath, Subrata Roy, Synthesis and characterization of Li Mn_{2-X} Mg_X O_4 prepared by sol–gel synthesisCeram.-Silik. 54 (1) (2010) 38–46.

[15] R Egli, W. Lowrie, Anhysteretic remanent magnetization of fine magnetic particles, J. Geophys. Res. 107 (B10) (2002) 2209. http://dx.doi.org/10.1029/2001 JB000671.