Magnetic and dielectric properties of nanophase lithium-substituted manganese-zinc ferrite

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Abstract. Nanocrystalline lithium-substituted manganese-zinc ferrites $Li_{0.5x}Mn_{0.4}Zn_{0.6-x}Fe_{2+0.5x}O_4$ were prepared by the sol-gel autocombustion method. X-ray diffraction analysis (XRD) confirmed that samples are monophasic and that only spinel phase is present. The saturation magnetization increases while the cell parameter of the cubic phase decreases with Li concentration. Magnetic permeability and dielectric permittivity of all samples were measured at room temperature as a function of frequency. Reflection loss calculations show that the prepared samples are good electromagnetic wave absorbers in microwave range. Li substitution plays an important role in changing the structural and magnetic properties of these MnZn ferrites.

Introduction

Polycrystalline ferrites have very good electrical properties that are dependent on several factors such as the preparation method, substitution with different cations and grain structure or size. Li and Li-substituted ferrites have been found to be excellent materials in high density recording media, absorbers and microwave devices due to their low cost, high saturation magnetization, high Curie temperature and hysteresis loop properties, which offer advantageous performance over other spinel structures [1-4]. They are used in microwave applications due to their high resistivity and low eddy current losses [5]. However, no reports have been found in the literature on microwave properties of MnZn substituted Li ferrites. In the present work, the influence of lithium substitution on structural, magnetic and dielectric properties of $Li_{0.5x}Mn_{0.4}Zn_{0.6-x}Fe_{2+0.5x}O_4$ ($0.0 \leq$ x ≤ 0.4), prepared by the citrate precursor method, is reported. To our knowledge, this LiZnMn-ferrite composition has not been reported yet.

Experimental

In the present work, analytical grade Li_2CO_3, $Mn(CH_3COO)_2.4H_2O$, $Fe(NO_3)_3.9H_2O$, $Zn(CH_3COO)_2. 2H_2O$, HNO_3 and citric acid were used to prepare LiZnMn-ferrites by the auto-combustion of a citrate precursor [6]. Samples with overall composition $Li_{0.5x}Mn_{0.4}Zn_{0.6-x}Fe_{2+0.5x}O_4$ ($0.0 \leq$ x ≤ 0.4) were prepared by dissolving Li_2CO_3 in concentrated nitric acid until a clear solution was obtained. The final mixture was slowly evaporated until a highly viscous gel was formed. At this stage, gelating reagent, ethylene glycol was added. The resulting gel was heated at T ~200ºC, when it ignited in a self-propagated process. The final residue was calcined at 1100 ºC for two hours in nitrogen flow. The samples were structurally characterized by X-ray diffraction with a Philips diffractometer equipped with a copper X-ray tube. Crystallite sizes were calculated from the FWHM of the (311) reflection using the Scherrer formula corrected for instrumental broadening. Cell parameters were calculated from X-ray patterns using the program Powder Cell. The morphology of the powder samples was examined by scanning electron microscopy (SEM) with a Zeiss DSM 982 GEMINI. Magnetic measurements were performed at room temperature using a LakeShore 7300 vibrating sample magnetometer with maximum applied field of 15 kOe. Curie temperature Tc was determined using a differential calorimeter SDT Q600 (TA Instruments) in N_2 atmosphere and under magnetic field. The heating rate was 10º/min. Complex permeability ($\mu'+i\mu''$)

of toroids and complex permittivity ($\varepsilon' + i\varepsilon''$) of pellets were measured on a HP4291A Material Analyser from 1-1800 MHz.

Results and Discussion

Fig. 1 shows the diffraction patterns of the series $Li_{0.5x}Mn_{0.4}Zn_{0.6-x}Fe_{2+0.5x}O_4$, for x=0.0 to 0.4. No secondary phases are detected −the observed peaks correspond only to the spinel phase. A monotonous displacement of the peaks position to higher angles is observed (shown in the inset of Fig. 1 for the (511) reflection) indicating a decrease in the cell parameter. This was confirmed after refining the spectra, obtaining cell parameters ranging from 8.446(1) Å for x=0.0 to 8.390(1) Å for x=0.4 (Table 1). The observed decrease in the lattice parameter with increasing substitution can be explained based on the relative ionic radius. As the ionic radius of Li^+ ions (0.78 Å) and Fe^{3+} ions (0.67 Å) are smaller than the ionic radius of Zn^{2+} (0.82 Å), the lithium and extra iron incorporated in both the tetrahedral and octahedral sites causes the decrease in the lattice constant [7].
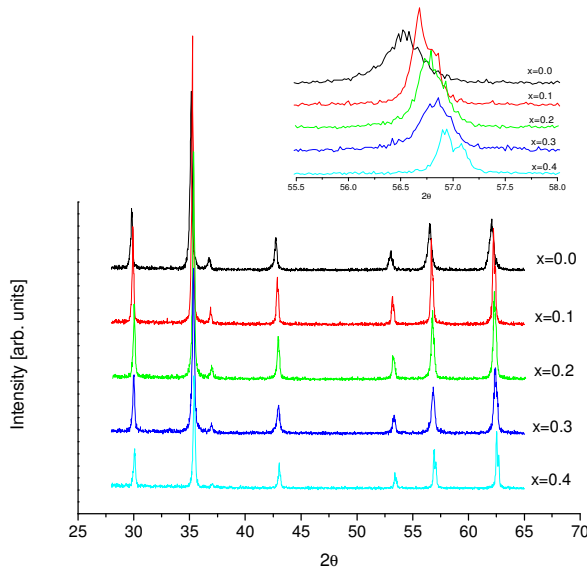

Figure 1: X-ray diffraction patterns of the series $Li_{0.5x}Mn_{0.4}Zn_{0.6-x}Fe_{2+0.5x}O_4$, for x=0.0 to 0.4. All the peaks correspond to reflections of the ferrite, with no extra reflections of secondary phases. The inset shows a slight displacement to higher angle which occurs for all the peaks.

Table1: Cell parameters, crystal size, saturation magnetization (Ms) and Curie temperature (Tc) for samples with different Li content.

$Li_{0.5x}Mn_{0.4}Zn_{0.6-x}Fe_{2+0.5x}O_4$	Cell parameter [± 0.001Å]	DRX crystal size [nm]	SEM crystal size [nm]	Ms [emu/g]	Tc [± 5 ℃]
x=0.0	8.446	100	200	48.8	180
x=0.1	8.425	75	190	74.4	182
x=0.2	8.419	73	190	87.5	194
x=0.3	8.410	72	170	91.1	196
x=0.4	8.390	70	170	92.7	176

SEM images of powders calcined at 1100°C for 2 hours show agglomerated particles with mean sizes that slightly decrease with Li substitution in the range of 200 nm to 170 nm (Fig.2a and b)
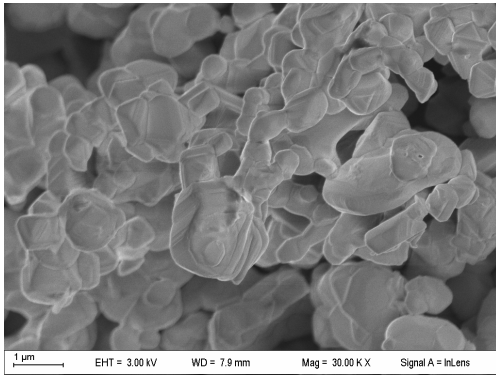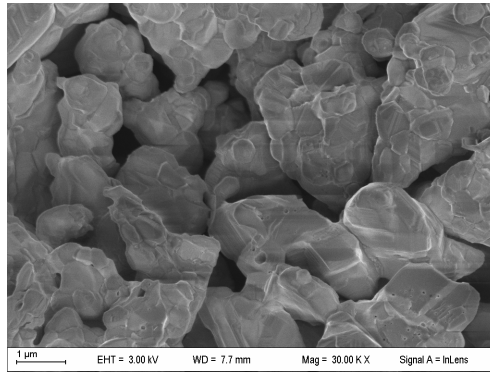
Fig.2 a) SEM image of $Mn_{0.4}Zn_{0.6}Fe_2O_4$

b) SEM image of $Li_{0.2}Mn_{0.4}Zn_{0.2}Fe_{2.2}O_4$
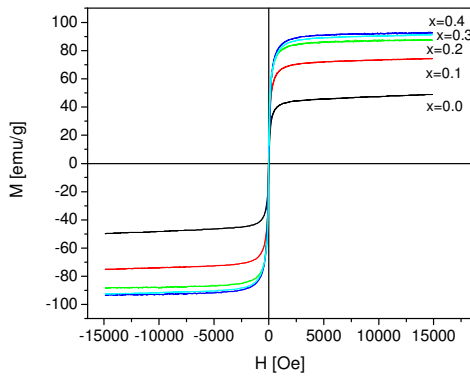
Figure 3: Hysteresis loops of the series $Li_{0.5x}Mn_{0.4}Zn_{0.6-x}Fe_{2+0.5x}O_4$, for x=0.0 to 0.4.

Hysteresis loops of the series $Li_{0.5x}Mn_{0.4}Zn_{0.6-x}Fe_{2+0.5x}O_4$, for x=0.0 to 0.4 are shown in Fig. 3. Saturation magnetization Ms is considerably modified by Li doping since its value increases from 48.8 emu/g for x=0.0 to 92.7 emu/g for x=0.4 (see Table 1 and Fig. 3). The inclusion of Li^+ and extra Fe^{3+} in the lattice promotes a cation arrangement between tetrahedral and octahedral sites that increases Ms to rather high values. Coercivity is low in every case; the sample with x=0.0 has a value of 30 Oe while all the samples with x≠0 have a coercivity of ~10 Oe. Similar values have been reported for MnZn ferrites [8]. The Curie temperature Tc of the samples was determined with the aid of TG measurements under an applied magnetic field. The ferro to paramagnetic transition could be noticed as a step in the weight vs temperature curves. The values for all the samples are indicated in Table 1. An increase in Tc is observed with increasing substitution up to x=0.3. This is not surprising as Tc of $Li_{0.5}Fe_{2.5}O_4$ is 670°C [9]. For x=0.4 a decrease of 20°C in Tc is detected, reaching 176°C. This can be explained considering the magnetic superexchange interaction and the following cation distribution. It is widely accepted that Zn^{2+} ions only occupy tetrahedral sites while Mn and Fe occupy both tetrahedral and octahedral sites [9]. However, for Li^+ ions both sites can be considered [7]. The AB interaction dominates the AA and BB interaction and the strength of AB interaction is given by Fe_A^{3+}–O^{2-}– Fe_B^{3+} linkages per formula unit. With Li substitution, the iron content increases, and there are more Fe_A^{3+}–O^{2-}– Fe_B^{3+} linkages. Hence higher values for Tc are expected for higher substitution (Table 1). For x> 0.3, a different cation arrangement can modify the exchange interaction and a fall in the Curie temperature is observed.

The complex relative permeability spectra of some LiMnZn ferrites are shown in Fig.4. It is well accepted that there are two mechanisms responsible for the shapes of permeability spectra: domain-wall movement and spin rotation. The samples prepared by the citrate precursor method have smaller grain-size than those prepared by the conventional method, and hence lower permeability due to spin rotation [9]. The real part of permeability increases with Li content. Permeability is related to Ms and to the anisotropy constant. Both parameters are modified with Li inclusion (Table 1). The microwave permittivity spectra (ε´) of these samples (not shown) indicate that the real parts do not change with frequency in the studied range. The ε´ values increase from 2.3 to 4.6 for x=0 to

x=4. There are two mechanisms responsible for the permittivity dispersion: electron polarization and ion polarization. Novikoa [10] has pointed out that there is a strong correlation between the conduction mechanism (hopping) and the dielectric behavior of ferrites. By electronic exchange, $Fe^{3+} \rightarrow Fe^{2+}$ and $Mn^{2+} \rightarrow Mn^{3+}$, local electrons displacements determine the polarization of the ferrites. Conductivity experiments of these samples are in progress.
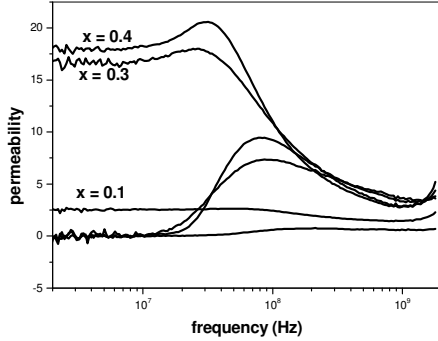

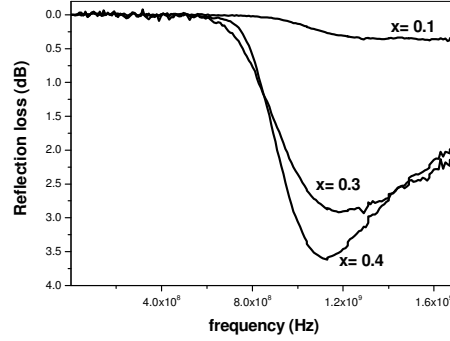Figure 4. Permeabilty of $Li_{0.5x}Mn_{0.4}Zn_{0.6-x}Fe_{2+0.5x}O_4$ 1MHz-1.8GHz

Figure 5. Calculated absorption spectra of $Li_{0.5x}Mn_{0.4}Zn_{0.6-x}Fe_{2+0.5x}O_4$

In this frequency range the reflection loss (R_L) is calculated as

$$R_L(dB) = 20\log|Z_{in} - 1|/|Z_{in} + 1|,$$

(1)

where Z_{in} is the normalized input impedance in free space

$$Z_{in} = \sqrt{\mu_r/\varepsilon_r} \tanh\left[-i(2\pi/c)\left(\sqrt{\mu_r \varepsilon_r}\right)fd\right]$$

(2)

where μ_r and ε_r are the relative complex permeability and permittivity of the absorber medium, f and c are, respectively, the frequency of microwave in free space and the velocity of light, d is the sample thickness [11]. Using the experimental values of the complex permeability and permittivity (Eq.1 and Eq.2), it is possible to estimate the absorption properties (Fig. 5). All the substituted samples exhibit the potential of relative wide band absorption (300Hz) in the frequency region from 1.0-1.3 GHz. The highest value of R_L is for the maximum Li substitution (x=0.4).

Conclusions

LiMnZn ferrites were successfully prepared by citrate precursor method. XRD confirms the spinel phase for all compositions with no secondary phases. Saturation magnetization increases with Li substitution. Lithium inclusion enhances microwave absorption with a maximum reflection loss of 3.7 dB at 1.1GHz for x=0.4.

References

[1] J. Qiu, L. Lan, H. Zhang, M. Gu, J. All. Comp. 453 (2008) 261.
[2] P. P. Hankare, R. P. Patil, U. B. Sankpal, S. D.J adhav, I. S. Mulla, K. M. Jadhav, B. K. Chougule, J. Mag. Magn. Mater. 321 (2009) 3270.
[3] S. Sugimoto, K. Haga, T. Kagotani, K. Inomata, J. Magn. Mag. Mat. 290-291 (2005) 1188.
[4] C. Sun, K. Sun, Phys. B 391 (2007) 335.
[5] B. Ramesh, D. Ravinder, Matter. Lett. 62 (2008) 2043.
[6] S. E. Jacobo, E. Sileo, R.Rotelo, Phys. B, 320/1-4 (2002) 257.
[7] H.Demidzu, T.Nakamura, Y.Yamada, J. Magn. Magn. Mater. (2010) doi: 10.1016/j.jmmm.2009.12.033.
[8] H. Shokrollahi, J. Magn. Magn. Mater. 320 (2008) 463.
[9] H. Smit, P. Wijn, Ferrites (1958).
[10] L. I. Rabkin, Z. I. Novikova, Ferrotes, Izs. Acad. Nauk. BSSR. Minsk (1960) 146.
[11] S.M. Abbas, A.K. Dixit, R. Chatterjee and T.C. Goel, J. Magn. Magn. Mater. 309 (2007) 20