Iraqi Journal of Physics, 2011 *Vol. 9, No.14, PP. 6 - 12*

Frequency Dependence of AC Resistivity and Dielectric Behavior of Lithium-Manganese Soft Ferrites

Muthafar F. Al-Hilli

Department of Physics, College of Science, University of Baghdad, Jaderiyah Campus, Baghdad, Iraq.
E-mails: mfj972@yahoo.com; m.alhilli@scbaghdad.edu.iq

Abstract

Lithium–Manganese ferrites having the chemical formula ($Li_{0.5-0.5x}$ Mn_x $Fe_{2.5-0.5x}$ O_4), ($0 \leq x \leq 1$) were prepared by double sintering powder processing. The density of the ferrite increased with Mn content while the porosity was noticed to decrease. The dielectric constant was found to increase at high frequencies more rapidly than the low ones. The dielectric constant found to decrease with Mn content. The decrease in loss factor with frequency agreed with Deby's type relaxation process. A maximum of dielectric loss factor was observed when the hopping frequency is equal to the external electric field frequency. Manganese substitution reduced the dielectric loss in ferrite. The variation of tanδ with frequency shows a similar nature to that of ε'' with frequency. The resistivity found to decrease with frequency, and this behavior with frequency was discussed according to Koop's theorem. Maximum resistivity was obtained at x = 0.8 doping level of Mn.

Keywords
Mn-Li ferrites,
Dielectric properties,
AC resistivity.

Article info
Received: Mar. 2010
Accepted: Apr. 2010
Published: Jan. 2011

دراسة الأعتمادية على التردد للمقاومة المتناوبة والسلوك العزلي لفيرايت الليثيوم - منغنيز

مظفر فؤاد جميل الحلي
قسم الفيزياء- كلية العلوم- جامعة يغداد

الخلاصة

تم تحضير فيرايت الليثيوم- منغنيز ذو الصيغة الكيميائية $Li_{0.5-0.5x}$ Mn_x $Fe_{2.5-0.5x}$ O_4 حيث ان $0 \leq x \leq 1$ وذلك باستخدام تكنولوجيا المساحيق. لوحظ بان كثافة الفيرايت المحضر كانت تزداد مع زيادة محتوى المنغنيز، بينما كانت المسامية تنقص مع زيادة محتوى المنغنيز. لقد وجد ان ثابت العزل الكهربائي يزداد مع التردد عند الترددات العالية بشكل اكبر مما هو الحال عند الترددادت الواطئة. وكان ثابت العزل الكهربائي ينقص مع زيادة نسبة المنغنيز في الفيرايت. النقصان في معامل الفقد العزلي كان مطابق لعملية الاسترخاء من نوع ديباي. والقيمة العظمى لمعامل الفقد وجدت عندما تساوى تردد قفز حاملات الشحنة مع تردد المجال الكهربائي الخارجي المسلط. عملية الاشابة لفيرايت اللثيوم بالمنغنيز وجدت انها تقلل من الفقد العزلي للفيرايت. وقد وجد بان سلوك التغيير في قيمة ظل زاوية الفقد tanδ مع التردد كان مشابه لسلوك الفقد العزلي. المقاومة الكهربائية كانت تنخفض مع زيادة التردد، وقد تمت مناقشة هذا التغيير حسب نظرية كووب، حيث ان القيمة العظمى للمقاومة كانت تقع عند قيمة اضافة $x=0.8$ من المنغنيز.

Introduction

Ferrites are mixed metal–Fe oxides adopting a variety of structures which have been used as ceramic ferrimagnetic materials in the electronics industry for more than fifty years. More recently, lithium transition metal oxides with spinel-related structure have been studied for their potential use as a stable host framework for cathode electrodes materials in lithium-ion rechargeable batteries [1, 2]. Low cost, ease of fabrication, high Curie temperature and better temperature stability of magnetic saturation for lithium ferrites have made them attractive from commercial point of view and are good substitutes of garnets

($Y_3Fe_5O_{12}$) for microwave devices, such as isolators, circulators and gyrators. The magnetic properties of lithium ferrite may be improved by the addition of small amounts of other cations, e.g., Mn, Cr or Al ions. The substitution with manganese and chromium ions reduces the 1:3 cations ordering in the solid solution series of $LiM_xFe_{5-x}O_8$, and the "disordered" ($Fd\bar{3}m$) spinel forms with the increasing M^{3+} content, while aluminum ions do not influence the "ordered" ($P4_132$) structure in the whole range of solid solutions [3]. Compounds with spinel structure in the quasi-ternary system "$LiO_{0.5}$-MnO_x-FeO_x" belong to group of important ceramic materials in the electronics and electrical industry. Thus lithium manganese spinel oxides $Li_{1+x}Mn_{2-x}O_4$ ($x \geq 0$) are of interest as lithium insertion electrodes for rechargeable batteries. For such applications, the migration ability of the lithium ions in the spinel framework as well as the possibility of different oxidations states of manganese plays a crucial role. On the other hand, both lithium and manganese ferrite are used as controllable components in the microwave engineering and partially substituted manganese ferrites are useful as core materials of high- frequency inductors and transformers in high - frequency engineering. These applications require materials with excellent soft magnet properties and small electrical losses [4]. Ferrites are also used as microwave absorbers. Some ferrites absorb microwave by losing interaction of the electric and magnetic field vector of incident waves and in the process transfer microwave energy into thermal energy. These materials possess an imaginary part of permittivity that can vary with composition of material and frequency [5]. The aim of the present work is to prepare Li-Mn mixed ferrite with low dielectric loss suitable for microwave applications.

Experimental

Lithium–Manganese ferrites having the chemical formula ($Li_{0.5-0.5x}Mn_xFe_{2.5-0.5x}O_4$), where (x= 0, 0.2, 0.4, 0.6, 0.8, 1) were prepared by double sintering powder processing. A proper ratios of analytical grade materials; Fe_2O_3, MnO and Li_2CO_3 were mixed in acetone for 2 hours using a ball mill. The mixed powders were pre-sintered at 900 ^oC for 2 h in air, and then remixed to increase the homogeneity. The samples were prepared by uniaxial powders pressing technique. The final sintering was carried out at 1100 ^oC with soaking time of 2 hours using Carbolite muffle furnace. The Seebeck coefficient was determined by the thermo emf measurements using Keithley 616 digital electrometer and power supply phywe 7475. The dielectric measurements and DC conductivity were carried out at room temperature using 4274A and 4275A Multi-Frequency LCR Meter HEWLETT-PACKARD. The samples density and porosity were measured accurately by the hydrostatic method using Archimedes principle [ASTM test methods (20-83, 493-70)].

Results and Discussion

Fig.1 shows a plot of the bulk density versus manganese content (x). It can be seen from the figure that the bulk density increases with manganese content. This confirms that the addition of manganese to lithium ferrites tends to densify material. A similar observation was also observed by several researches in various ferrite systems [2, 6]. The porosity was found to decrease with Mn content (x) as given in Table 1. It’s may be because Mn acts as a fluxing agent in the ferrite body, which increased the material compaction.

The Seebeck coefficient (S) was determined using the relation

$$S = \frac{\Delta E}{\Delta T} \dots\dots\dots (1)$$

where (ΔE) is the thermo e.m.f. produced across the sample due to the temperature difference (ΔT) [7].

The Seebeck coefficient results as shown in Table 1 are all with a negative sign indicating that the electrons are the majority charge carriers. On the bases of its negative sign, the manganese doped lithium ferrites may be classified as n-type semiconductors. Thus, the conduction mechanism for n-type ferrites is predominantly due to hopping of electrons from Fe^{2+} to Fe^{3+} ions:

$Fe^{3+} + e^{-} \leftrightarrow Fe^{2+}$

According to Srinivasan and Srivastava [8] the Seebeck coefficient for cubic spinel system is given by:

S = (total number of iron ions on B-site/total number of Fe^{2+} ions on B-site).

Therefore an increase in S on addition of Mn may suggest that addition of Mn ions has an effect of reducing the number of Fe^{2+} ions on B-site.

The values of carrier concentration (*n*) obtained from thermoelectric power coefficient data using the following equation

$$n = N\, exp\left(-\frac{Se}{k}\right) \ldots\ldots\ldots (2)$$

where (k) is the Boltzmann constant, (e) is the electron charge, (n) is the charge carrier concentration and (N) is the density of states in the conduction band or of the electronic levels involved in the conduction process. Semiconductors of low mobility such as ferrites which have exceedingly narrow bands or localized levels, the value of the density of states (N) can be taken as ($10^{22} cm^{-3}$). The values of carrier concentration were calculated by substituting the absolute value of Seebeck coefficient in eq. (2) [9, 10]. The decrease in charge carrier concentration with Mn addition supports the suggestion that Mn ions reduce the number of Fe^{2+} ions on B-site. If the ferrite under study is assumed to be predominately due to only one type of charge carriers, the mobility μ of the charge carriers is given by the well known relation

$$\sigma = ne\mu_e \ldots\ldots\ldots (3)$$

where ($\mu_e \gg \mu_h$), μ_e is the mobility of electrons, μ_h is the mobility of halls and (σ) is the electrical conductivity of the sample at the given temperature. The mobility of charge carriers was calculated from the conductivity using eq.(3). The value of mobility found to be very low when compared to normal semiconductors. However, in case of ferrites such low values of mobility are have been reported by several works [11, 12, 13]. The electrical conductivity was found to increase with mobility increase. Thus, the conductivity here is governed by the mobility rather than the charge carrier concentration.

The effect of frequency (f) on the real part of dielectric constant (ε') is illustrated in Fig. 2. The dielectric constant is found to remain constant at low frequencies. At higher frequencies, the dielectric constant shows a maximum (abnormal behavior) then decreases with frequencies increase with another maximum at higher frequencies, showing the usual dielectric dispersion. This peak in dielectric constant (ε'_{max}) was observed for CuNi ferrite, CuZn ferrite, CuCd ferrite and for NiAl ferrite. In normal dielectric behavior the dielectric constant decreases with increasing frequency until it reaches a nearly constant value because beyond a certain frequency of the electric field, the electronic exchange cannot follow the alternating field, so it reaches a constant value. The behavior of the ferrite under study showed an abnormal behavior, which can be explained in the light of the Rezlescu model. According to this model the polarization process in the ferrite is similar to the conduction process. By the electronic exchange $Fe^{2+} \leftrightarrow Fe^{3+}$, local displacements of electrons are obtained in the direction of the applied field. These displacements determine the polarization in the ferrites. In the ferrites containing Cu and Ni an exchange of $Cu^{1+} \leftrightarrow Cu^{2+}$ and $Ni^{2+} \leftrightarrow Ni^{3+}$, also exists. The Cu^{1+} causes an important modification of the electrical and magnetic properties of the ferrite. It was shown that the copper ferrites exhibit p-type electrical conduction via the moving holes ascribed to the reduction tendency of the $Cu^{2+} \leftrightarrow Cu^{1+}$ ions at 900-950 ^{o}C during the sintering process. The abnormal dielectric behavior of the Cu ferrites is due to the collective contribution of the two types of carriers, p and n, to the polarization. The contribution of the p-type carriers is lower than that obtained by the electronic exchange and it has an opposite sign. In addition, since the mobility of the p-type carriers is lower than that of the n-type carriers, their conduction to polarization will decrease more rapidly. By assuming the contribution of both types of carriers to the polarization, one expects the behavior of the dielectric constant as a function of frequency [14]. In the present ferrite, the experimental results agree with this model. The p-type conduction may result from the exchange between $Mn^{2+} \leftrightarrow Mn^{3+}$ ions, causing an abnormal behavior of the dielectric constant. However, the dispersion of dielectric constant with frequency is due to Maxwell–Wagner type interfacial polarization in agreement with Koop's phenomenological theory. The polarization in ferrite is through a mechanism similar to the conduction process. The presence of Fe^{3+} and Fe^{2+} ions has rendered ferrite materials dipolar. Rotational displacement of dipoles results in orientational polarization. In ferrites, the rotation of $Fe^{2+} \leftrightarrow Fe^{3+}$ dipoles may be visualized as the exchange of electrons between the ions so that the dipoles align themselves in response to the alternating field. The existence of inertia to the charge movement would cause relaxation of the polarization. The polarization at lower frequencies may result from electron hopping between $Fe^{3+} \leftrightarrow Fe^{2+}$ ions in the ferrite lattice. The polarization decreases with increase in frequency and reaches a constant value due to the fact that beyond a certain frequency of external field the electron exchange $Fe^{3+} \leftrightarrow Fe^{2+}$ cannot follow the alternating field. In general the dielectric constant increased with Mn content may be due to the various contributions to the polarizations [15, 16].

The dielectric loss factor (ε'') versus frequency (f) is shown in Fig.3. The decrease in (ε'') with increasing frequency agrees well with Deby's type relaxation process [17]. The conduction mechanism was explained in terms of the hopping conduction process, which occurs among the octahedral B-sites. In this case, a maximum in ε'' is observed when the hopping frequency is equal to the external electric field frequency. The predominant losses in ferrites are due to hysteresis and eddy current losses at operating frequency lower than the relaxation frequency of wall displacement. The hysteresis loss depends on many parameters like magnetostriction constant, magneto-crystalline anisotropy, saturation magnetization and microstructure. The eddy current loss mainly depends on the electrical resistivity of the ferrite [18]. So, it may be consider that the lowering of loss factor in Mn-substituted compositions resulted mainly from a reduction in eddy current loss due to their higher electrical resistivity. The dielectric loss tangent ($\tan\delta$) dependence upon frequency is shown in Fig.4. The loss factor at low frequencies is considered to be caused by domain wall resonance. At higher frequencies, losses are found to be low, since the domain wall motion is inhibited and magnetization is forced to change by rotation. The peaking behavior occurs when the jump frequency of electrons between Fe^{2+} and Fe^{3+} is equal to the frequency of the applied field [19].

The electrical resistivity as a function of frequency is shown in Fig.5 at different Mn content (x). The resistivity (ρ) decreased with frequency (f) increase, according to the relation [20]:

$$\rho = \frac{1}{\omega\, \varepsilon_o \varepsilon''} = \frac{1}{\omega\, \varepsilon_o \varepsilon' \tan\delta} \quad \ldots\ldots\ldots (4)$$

where ω=2πf is the angular frequency, ε_o is the vacuum permittivity. This behavior with frequency can be explained by Koop's theorem, which supposed that the ferrite compact acts as a multilayer capacitor. In this model, the ferrite grain and grain boundaries have different properties. The effect of the multilayer capacitor increases with frequency; as a result the resistivity decreases [21]. The maximum resistivity was found to be at x=0.8 at low frequencies. However, at higher frequency the difference in resistivity with different x become very low and the resistivity reaches to constant value.

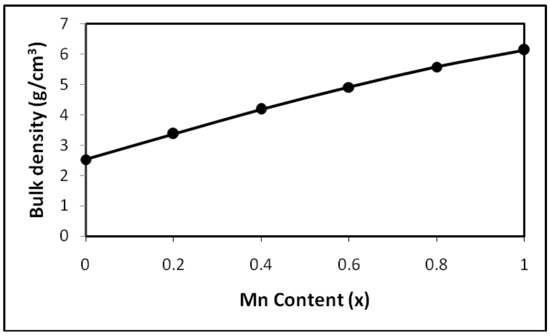

Fig.1. Plot of bulk density versus manganese content (x).

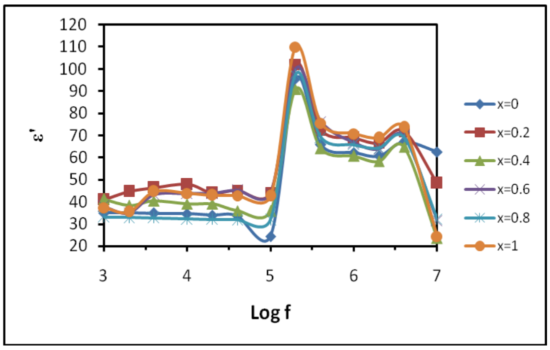

Fig.2. Behavior of dielectric constant versus Log frequency for $Li_{0.5-0.5x}Mn_xFe_{2.5-0.5x}O_4$.

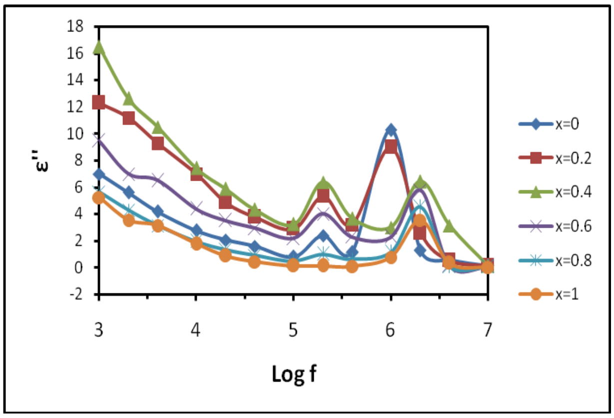

Fig.3. Dependence of dielectric loss factor upon Log frequency for $Li_{0.5-0.5x}Mn_xFe_{2.5-0.5x}O_4$.

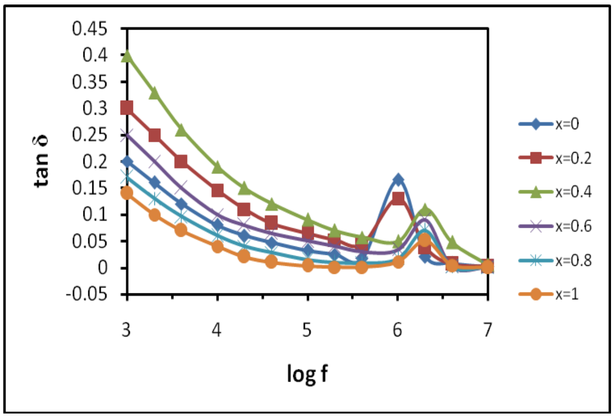

Fig.4. change of dielectric loss tangent (tanδ) with Log frequency for $Li_{0.5-0.5x}Mn_xFe_{2.5-0.5x}O_4$.

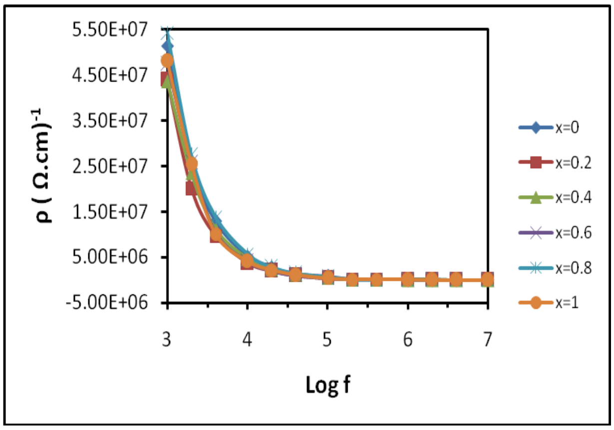

Fig.5. Plot of AC Resistivity versus Log frequency for $Li_{0.5-0.5x}Mn_xFe_{2.5-0.5x}O_4$.

Table1. The effect of Mn content (x) on the porosity %, Seebeck coefficient (S), carrier concentration (n), electrical conductivity (σ) and mobility (μ) measured at room temperature.

Mn content (x)	Porosity %	Seebeck coefficient (S) (μV/K)	Carrier concentration (n) (10^{21} /cm^2)	Electrical Conductivity (σ) (Ω^{-1}.cm^{-1})	Mobility (μ) (cm^2/V.s) 10^{-10}
0	6.824	- 22.35	7.626	1.363	1.117
0.2	6.431	- 34.58	6.576	1.749	1.662
0.4	6.021	- 48.95	5.524	1.363	1.542
0.6	5.565	- 59.04	4.888	2.609	3.335
0.8	5.117	- 63.47	4.633	2.075	2.799
1	4.742	- 65.61	4.514	1.897	2.627

Conclusions

A series of Mn modified lithium ferrite were prepared by double sintering powder processing method. The density of Mn modified lithium ferrites was strongly influenced by the Mn content. The Seebeck coefficient results confirmed that the predominant conduction mechanism is by hopping of electrons from Fe^{2+} to Fe^{3+} ions. The conductivity was found to be governed by the mobility rather than the charge carrier concentration. The dielectric constant change with frequency is due to Maxwell–Wagner type interfacial polarization in agreement with Koop's phenomenological theory. While the abnormal behavior of the dielectric constant with frequency is due to the exchange between $Mn^{2+} \leftrightarrow Mn^{3+}$ ions which obey the Rezlescu model. The lowering of loss factor in Mn-substituted ferrites resulted mainly from a reduction in eddy current loss due to their higher electrical resistivity. The study provides important information on tailoring the electrical and dielectric properties of Mn-substituted lithium ferrite in actual applications.

Acknowledgments

The author would like to thank the Department of Physics at the University of Baghdad and especially the Group of Thin Films for the support and assistance. Thanks are due to the University of Technology and Ministry of Sciences and Technology for the assistance.

References

[1] Mercedes Gracia, José F. Marco, J. Ramón Gancedo, Juan Luis Gautier, Edmundo I. Ríos, Nieves Menéndez and Jesús Tornero: J. Mater. Chem., 13 (2003), 844–851.

[2] D. Ravinder, L. Balachander and Y.C. Venudhar: Materials Letters, 49 (2001) 267–271.

[3] J. Darul: Acta Physica Polonica A, 114 (2) (2008), 367-373.

[4] C. Wende and H. Langbein: Cryst. Res. Technol., 41 (1) (2006), 18 – 26.

[5] Sukhleen Bindra Narang and I. S. Hudiara: Journal of Ceramic Processing Research, 7 (2006) No. 2, 113-116**.**

[6] Mansour AL-HAJ: Turk. J. Phys., 33 (2009) 185 – 192.

[7] D. Ravinder: Journal of Alloys and Compounds, 291 (1999) 208–214.

[8] A. M. Shaikh, C. M. Kanamadi and B.K. Chougule: Materials Chemistry and Physics, 93 (2005) 548–551.

[9] Muthafar F. Al-Hilli, Sean Li and Kassim S. Kassim: Materials Science and Engineering, B 158 (2009) 1– 6.

[10] V. Devender Reddy, M. A. Malik and P. Venugopal Reddy: Materials Science and Engineering, B 8 (1991) 295-301.

[11] Y. Purushotham, J. S. Chandel, S. P. Sud, V. K. Babbar, K. Venkat reddy and P. Venugopal Reddy: Materials Science and Engineering, B 34 (1995) 67-73.

[12] J. M. Song and J. G. Koh: Journal of Magnetism and Magnetic Materials, 152 (1996) 383-386.

[13] D. Ravinder and A. Chandra Shekhar Reddy: Journal of Alloys and Compounds, 353 (2003) 86–90.

[14] M. A. El Hiti, M. A. Ahmed, M. M. Mosaad and S. M. Attia: Journal of Magnetism and Magnetic Materials, 150 (1995) 399-402.

[15] M. A. Ahmed, E. Ateia, L.M. Salah, A.A. El-Gamal: Materials Chemistry and Physics, 92 (2005) 310–321.

[16] R. S. Devan, Y. D. Kolekar and B. K. Chougule: J. Phys. Condens. Matter, 18 (2006) 9809–9821.

[17] E. Ateia, M.A. Ahmed, A.K. El-Aziz: Journal of Magnetism and Magnetic Materials, 311 (2007) 545–554.

[18] P.K. Roy, Bibhuti B. Nayak and J. Bera: Journal of Magnetism and Magnetic Materials, 320 (2008) Issue 6, 1128-1132.

[19] R. G. Kharabe, R .S. Devan, C. M. Kanamadi and B. K. Chougule: Tech. Note, Smart Mater. Struct., 15 (2006) N36–N39.

[20] M.A. Ahmed, E. Ateia, S.I. El-Dek: Materials Letters, 57 (2003) 4256–4266.

[21] S.A. Mazen: Materials Chemistry and Physics, 62 (2000) 139–147.