IOP Conf. Series: Materials Science and Engineering **438** (2018) 012013 doi:10.1088/1757-899X/438/1/012013

Study of the Structural and Magnetic Properties of Li Substituted Cu-Mn Mixed Ferrites

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Abstract: A very fast auto-combustion reaction technique was applied for the preparation of a series of $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ ferrites in a wide range of composition (with x = 0.00, 0.10, 0.20, 0.30, 0.40 and 0.44). Disc and toroid shaped samples were prepared and sintered at various temperatures, in namely, 1200, 1250, 1300 ºC in air for 1 hour. The spinel structure of all these samples were confirmed by X-ray diffraction and grain size estimation obtained from the optical microscope. It has been found that the lattice constant increases linearly with increasing Li contents. The grain size increases with increasing Li content and sintering temperature in $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$. The magnetic properties of these compositions are characterized by high frequency (10 KHz-120 MHz) magnetic permeability measurements. The real part of initial permeability, $\mu_i^{/}$ increases with increasing Li content. It has also been observed that $\mu_i^{/}$ for each sample increases with sintering temperatures because of uniform grain growth. The relative quality factor, Q increases with increasing sintering temperature. Among all the samples, the highest value of Q-factor has been observed for x = 0.40 sintered at 1300 ˚C.

1. Introduction

Ferrites have been considered as extremely vital electronic materials for the greater part a century. It turns into the attractive research field for many researchers and advancement in this field is as yet going ahead, from basic as well as application perspective. The spinel ferrites are compound of iron oxides and transition metal oxides [1]. The physical properties of spinel ferrites are controlled by the preparation conditions, chemical compositions, sintering temperatures and amount of substitution [2]. In particular, lithium ferrite or mixed lithium ferrites have high potential for microwave applications, especially as a replacement of garnets, because of their low cost, squareness of the hysteresis loop, high Neel temperature (T_N), high resistivity, low magnetic and dielectric losses [3]. The Li-based ferrite is a standout amongst the most adaptable attractive materials for common use having numerous applications in both low and high frequency devices. It plays a crucial role in various technological applications, for example, microwave device, power transformer, rod -antennas, read-write heads for fast digital tapes [4, 5].

Recently, in our laboratory Hossain et. al [6] have studied the effect of Li substitution on the magnetic properties of $Li_xMg_{0.40}Ni_{0.60-2x}Fe_{2+x}O_4$ ferrites, prepared by the standard solid state reaction technique. It was observed that, the studied spinel ferrites are in ferrimagnetic state at room temperature and have a low saturation field. The real part of initial permeability ($\mu_i^{/}$) and relative quality factor (Q-factor), both found to be maximum at x = 0.25 for 1100 ºC. On the other hand, Hoque et. al. [7] have worked on Cu substituted Li-ferrite and reported that, the structural properties are strongly dependent on the sintering temperature due to the Jahn-Teller distortion of Cu^{2+}. An increase in initial permeability has been observed with the increase in Cu content but the resonance frequency shifts towards the lower frequency. Many researchers have investigated Li-Zn-Cu-Mn [8], Li-Cu-Co-Zn [4], Li-Mg-Mn [9], Li-Ni-Zn [10] and Li-Mn-Zn [11], ferrites. To the best of our knowledge, no published literature is

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available by other researchers on Li substituted $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ prepared by combustion technique. Therefore, there has been a growing eagerness on Li-substituted Cu-Mn ferrite for microwave applications and high permeability with low magnetic loss. In the present work, the $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ has been prepared through auto-combustion technique and sintered at various temperatures. The structural and magnetic properties have been studied as a function of compositions and temperatures.

2. Experimental

The Polycrystalline $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ (x = 0, 0.10, 0.20, 0.30, 0.40 and 0.44) ferrites were prepared by auto-combustion technique. The analytical grade of $LiNO_3$, $MnCl_2.4H_2O$, $Cu(NO_3)_2.3H_2O$ and $Fe(NO_3)_3.9H_2O$ were weighed according to the stoichiometric amount and dissolved in ethanol. The mixture was placed in a magnetic heating stirrer at 80 ºC, followed by an ignition, the combustion takes place within a few seconds and fine powders were precipitated. These powders were crushed and ground thoroughly. The fine powders of various compositions were then calcined at 900 °C for 5 h for the final formation of $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ ferrites. Then the fine powders are granulated using Polyvinyl Alcohol (PVA) as a binder and pressed into disk and toroid-shaped samples. The samples were sintered at various temperatures, in namely, 1200, 1250, and 1300 ºC in air for 1 hour.

3. Results and Discussions

3.1 Structural Properties

X-ray diffraction was carried out with an X-ray diffractometer (Model: D8 Advance, Bruker AXS) for each sample. The X-ray diffraction (XRD) was performed to verify the formation of spinel structure of various $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ ferrites, in which Mn^{2+} is replaced by Li^+ and Fe^{3+}. The XRD patterns of these Li^+ substituted $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ (with x = 0.00, 0.10, 0.20, 0.30, 0.40 and 0.44) ferrites sintered at 1200 ˚C in air for 1 h are shown in figure 1.

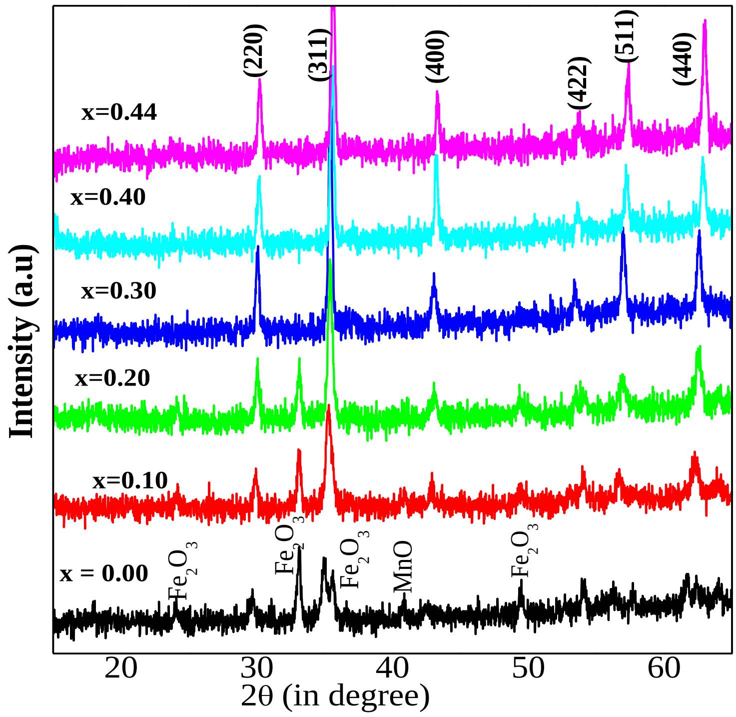

Figure 1. The X-ray diffraction patterns for $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$

The results indicated that these materials have a formation of cubic spinel structure for each composition. The values of lattice constant obtained from each plane are with the help of Nelson-Riley function [12]. Figure 2 shows that the lattice constant, a_0 as a function of lithium contents for various $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ sintered at 1200 °C.

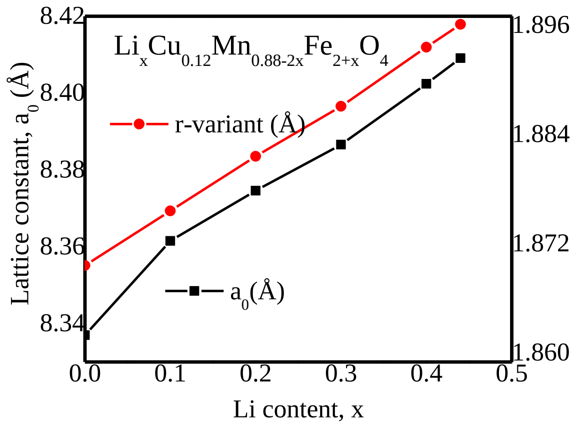

Figure 2. Variation of lattice constant with Li contents for $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ sintered at 1200 ºC.

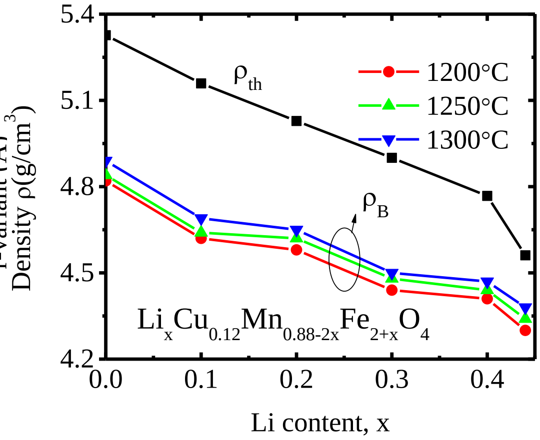

Figure 3. Variation of X-ray density and bulk density with Li contents, x for $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$

It is noticed that the lattice constant increases with increasing of Li^+ content in $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ ferrites. This increase of lattice constant can be attributed to the ionic size differences since the unit cell has to expand when substituted by ions with large ionic size. The ionic radius of Li^+ (0.68Å) is greater than that of Mn^{2+} (0.67 Å) [13-14]. When the larger Li^+ and Fe^{3+} ions enter the lattice, the unit cell expands while preserving the overall cubic symmetry. On the other hand, the bulk density ρ_B of each composition of $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ ferrites sintered at different temperatures was measured. The theoretical density, ρ_{th} of each sample was calculated and it is noticed that both ρ_{th} and ρ_B decrease with increasing Li substitution in $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ for constant sintering temperature. This phenomenon could be explained in terms of the atomic weight. The atomic weight of Mn (54.94 amu) is greater than combined atomic weight of the Li (6.941 amu) and Fe (55.845 amu) [13].

3.2 Magnetic properties

The optical micrographs have been taken by using optical microscope (Model: NMM-800TRF) of $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ for x= 0.40 are shown in figure 4 sintered at 1200, 1250 and 1300˚C, respectively. Average grain sizes (D) of all samples are determined from optical micrographs by linear intercept technique [14]. The D is significantly dependent on Li substitution. The D increases with increasing Li substitution for fixed sintering temperature. It is also observed that D increases with increasing sintering temperatures. The magnetic property, in particular, magnetic permeability of polycrystalline ferrite is related to two different type magnetizing mechanisms: spin rotation and domain wall motion [15-16], which can be described as, $\mu_i^/ = 1 + \chi_w + \chi_{spin}$, where χ_w is the domain wall susceptibility, χ_{spin} is intrinsic rotational susceptibility. χ_w and χ_{spin} may be written as:

$$\chi_w = 3\pi M_s^2 D / 4\gamma \tag{1}$$

and

$$\chi_{spin} = 2\pi M_s^2 / K_u \tag{2}$$

where M_s is the saturation magnetization, K_u is the total anisotropy, D is the grain diameter, and γ the domain wall energy. The initial magnetic permeability for each sample was measured by using Wayne Kerr Impedance Analyzer (Model: 6500B). The initial magnetic permeability, $\mu_i^/$ increases with increasing Li^+ content for different sintering temperatures (1200, 1250 and 1300 ˚C) in air as

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shown in figure 5. It is also observed that $\mu_i^{/}$ increases with increasing sintering temperature. The figure 6 shows that the $\mu_i^{/}$ and D as a function of Li content sintered at 1200 °C. According the Globus and Duplex model [17], the $\mu_i^{/}$ can be written as

$$\mu_i^{/} = \frac{M_s^2 D}{\sqrt{K}} \tag{3}$$

where M_s is the saturation magnetization and K is the magneto crystalline anisotropy constant. This increase in permeability is expected, because grain size of all samples increase with Li content. The large grains favor domain wall mobility, giving rise to high permeability. Therefore, the high values of initial permeability in the present samples can also be attributed to the high grain sizes of the samples. Moreover, the magnetic properties of soft ferrite are strongly influenced by it's composition, additives and microstructures of the material. Among all these factors, the microstructures have great influence on magnetic properties. It is generally believed that larger the grain sizes, the higher the magnetic initial permeability. The increasing value of $\mu_i^{/}$ with the increase of sintering temperature is due to the lower porosity for samples sintered at higher sintering temperature. As sintering temperature increases pores and voids are reduced with increasing sintering temperature.

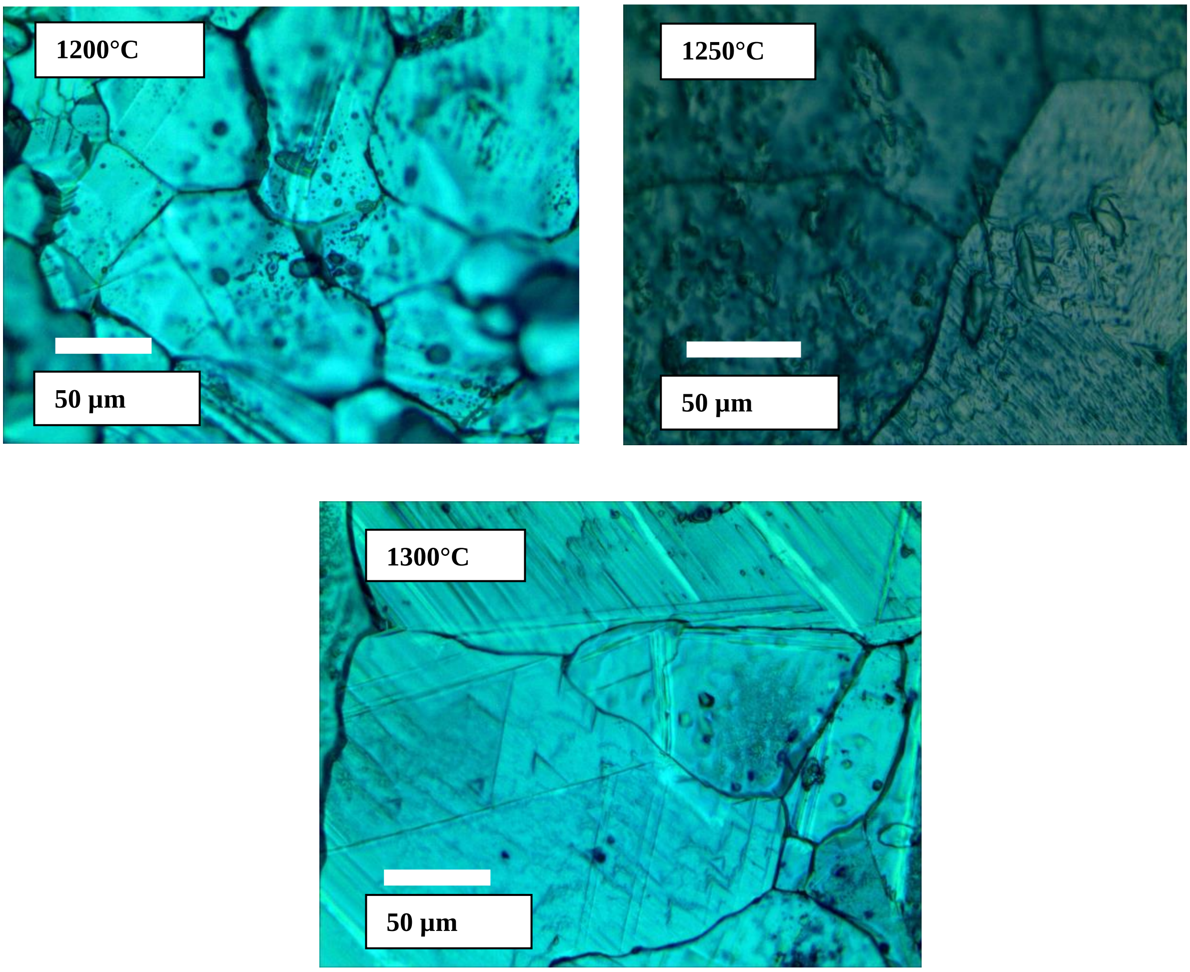

Figure 4. The optical micrographs of $Li_{0.4}Cu_{0.12}Mn_{0.08}Fe_{2.40}O_4$ sintered at different temperatures

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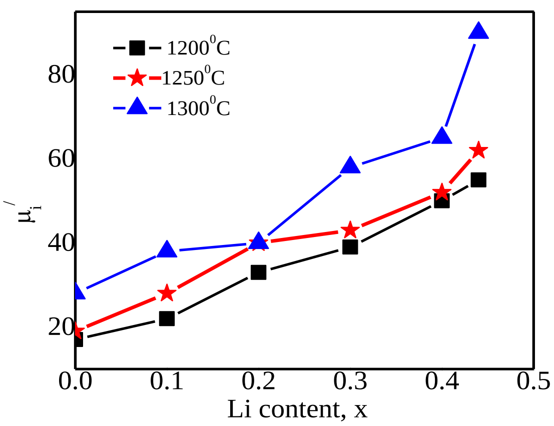

Figure 5: The initial magnetic permeability, $\mu_i^/$ with lithium content for $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ sintered at 1200, 1250 and 1300 ˚C in air

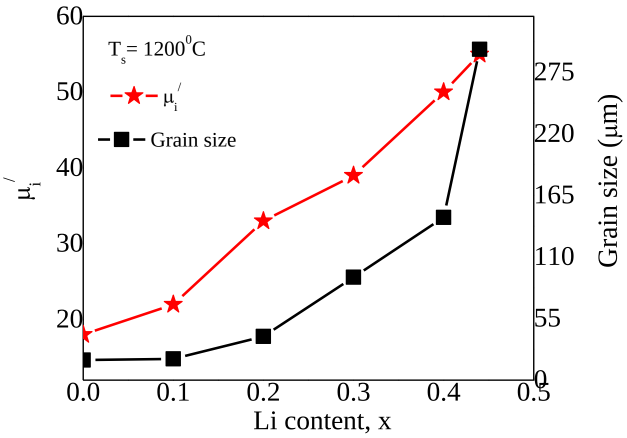

Figure 6: The initial magnetic permeability, $\mu_i^/$ and grain size, D as a function of Li content sintered at 1200 °C.

For functional application the relative quality factor (Q-factor) is frequently used as a measure of performance. The relative quality factor versus frequency plots of all the samples sintered at 1200, 1250 and 1300 ˚C are shown in figure 7. It can be seen that the value of *Q*-factor increases with an increase of frequency and shows a peak around 3 MHz. The Q increases with increasing sintering temperature. Among all the studied samples, highest value of Q-factor (=2165) is observed for $Li_{0.40}Cu_{0.12}Mn_{0.08}Fe_{2.40}$ sintered at 1300 ˚C.

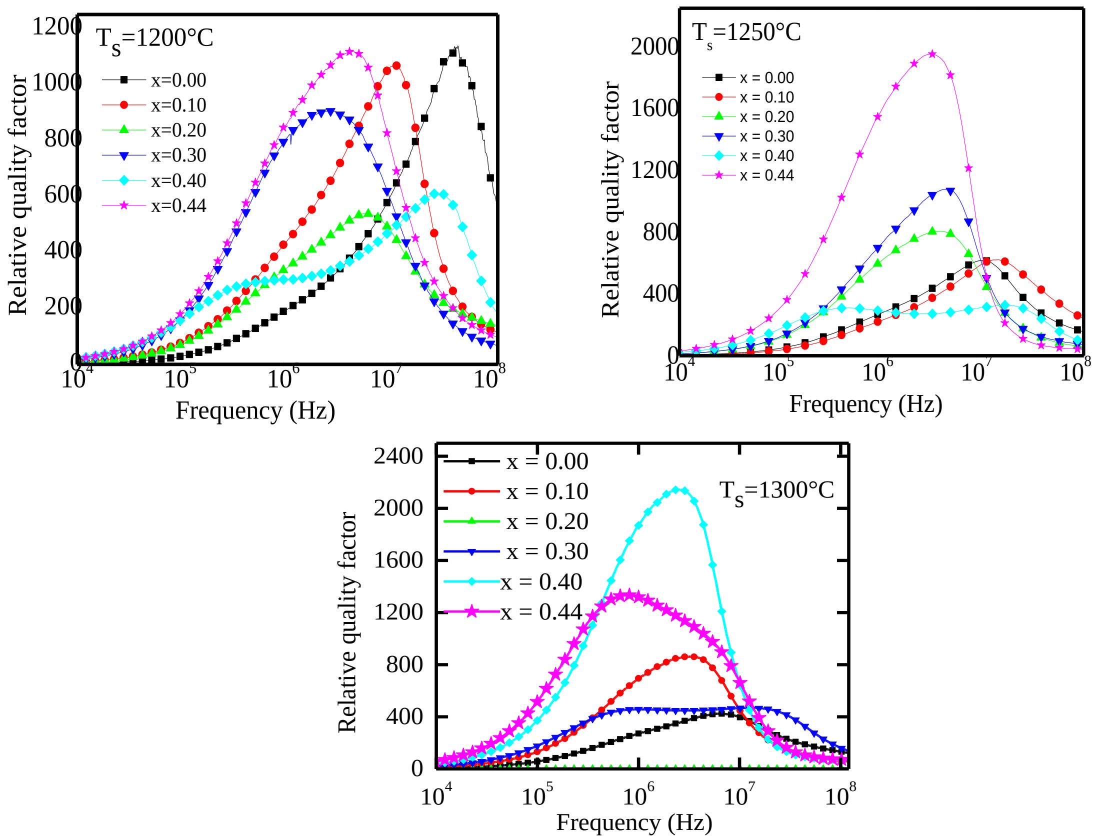

Figure 7. The variation of Q-factor with frequency for $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ sintered at 1200, 1250 and 1300 ˚C

4. Conclusions

The XRD patterns confirm that the samples are cubic spinel structure. The lattice parameter increases linearly with increasing Li content. This is due to greater ionic radius of Li ion than that of Mn ion. The study of microstructure shows that grain size increases with increasing Li content in $Li_xCu_{0.12}Mn_{0.88-2x}Fe_{2+x}O_4$ samples. The $\mu_i^{/}$ increases with increasing Li content for a fixed sintering temperature. The $\mu_i^{/}$ also increases with increasing of sintering temperatures for all samples because of the microstructure are homogeneous with large grain size and a uniform grain size distribution. The highest $\mu_i^{/}$ is observed for x = 0.44 which is about three times greater than that of parent composition for all sintering temperatures. The highest value of Q-factor is observed for x = 0.40.

Acknowledgments

The authors are grateful to Bangladesh University of Engineering and Technology for providing the financial support for this research. The authors are also thankful to Bangladesh Council of Scientific and Industrial Research for providing their laboratory facilities.

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