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# Structural and magnetic properties of Li–Cu mixed spinel ferrites

S. Manjura Hoque [a,*], M. Samir Ullah [b], F.A. Khan [b], M.A. Hakim [a], D.K. Saha [a]

[a] Materials Science Division, Atomic Energy Centre, Dhaka 1000, Bangladesh
[b] Department of Physics, Bangladesh University of Engineering and Technology, Dhaka 1000, Bangladesh

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ABSTRACT

$Li_{0.5-x/2}Cu_xFe_{2.5-x/2}O_4$ (where $x=0.0$–$1.0$) ferrites have been prepared by solid-state reaction. X-ray diffraction was used to study the structure of the above investigated ferrites at various sintering temperatures. Samples were sintered at 1000, 1100 and 1200 °C for 3 h in the atmosphere. For the sintering temperature of 1000 °C, $Li_{0.5-x/2}Cu_xFe_{2.5-x/2}O_4$ undergoes cubic to tetragonal transformation for higher Cu content. However, for the sintering temperature of 1100 and 1200 °C, X-ray diffraction patterns are mainly characterized by fcc structure, though presence of tetragonal distortion was found by other temperature dependence of initial permeability curves. The lattice parameter, X-ray density and bulk density were calculated for different compositions. Curie temperature was measured from the temperature dependence of initial permeability curves. Curie temperatures of Li–Cu mixed ferrites were found to decrease with the increase in $Cu^{2+}$ content due to the reduction of A–B interaction. As mentioned earlier, temperature dependence of initial permeability curves was characterized by tetragonal deformation for the samples containing higher at% of Cu. The complex initial permeability has been studied for different samples. The *B–H* loops were measured at constant frequency, $f=1200$ Hz, at room temperature (298 K). Coercivity and hysteresis loss were estimated for different Cu contents.



## 1. Introduction

Soft ferrites are used in different kinds of magnetic devices for high frequency applications [1–4]. Li-ferrites emerge as a good microwave device material due to their high Curie temperature, high squareness ratio, superior temperature stability of saturation magnetization, low intrinsic linewidth and low magnetic losses [5,6]. Magnetic properties of ferrites are strongly dependent on the crystal structure and cation distribution, which are governed by their sintering temperature and atmosphere, type and amount of substitution and/or doping and method of preparation [7]. Modifications in the properties of the lithium ferrite, $Li_{0.5}Fe_{2.5}O_4$, due to the substitution of various ions have been studied by several workers. Various studies can be found in the literature on Li–Ti, Li–Ge, Li–Cd and Li–Zn ferrites [8,9]. Most of these ferrites are of non-cubic structure at low temperatures and spinel at high temperatures [10]. Generally, $Li_{0.5}Fe_{2.5}O_4$ has face centered cubic inverse spinel structure in which all $Li^+$ ions and 3/5 of all $Fe^{3+}$ ions occupy the octahedral B sites whereas the remaining $Fe^{3+}$ ions occupy the tetrahedral A sites. $CuFe_2O_4$ is distorted inverse spinel and its tetragonal distortion has been explained by Jahn–Teller effect [11]. $Cu^{2+}$ is a $d^9$ cation and d orbitals are occupied by unpaired electrons, which render the magnetic moment of one Bohr magneton, whereas at higher temperatures there is a change in valence state from divalent to monovalent transition of Cu ions. $Cu^{1+}$ is a $d^{10}$ cation and d orbitals are completely filled, which gives zero magnetic moment. At higher temperatures tetragonal to cubic transition is also observed in $CuFe_2O_4$. Thus, Cu containing ferrites possess unique structural modifications, which are absent in other mixed spinel systems. There is scarcity of data on Cu substituted $Li_{0.5}Fe_{2.5}O_4$. In the present study the focus is on the investigation of copper substituted lithium ferrite to understand the structural and magnetic properties.

## 2. Experimental

$Li_2CO_3$, CuO and $Fe_2O_3$ of high purity were mixed homogeneously with appropriate ratio of cations and wet milled in a steel ball mill for 6 h. The samples were dried and the dried powder was pressed into disk shape. The disk shaped samples were pre-fired at 800 °C for 3 h in air to form ferrite through solid-state reaction. The raw ferrite was wet milled extensively to get fine powder. The powder was then dried and mixed with polyvinyl alcohol as a binder for granulation. Then the granulated powder was pressed into desired shapes using metal dies. Dies of several shapes were used for pressing. The pressed products were

* Corresponding author. Tel.: +88 02 8626603; fax: +88 02 8617946.
*E-mail address:* manjura_hoque@yahoo.com (S. Manjura Hoque).

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sintered at 1000, 1100 and 1200 °C in air for 3 h. Formation of ferrite was confirmed by Philips analytical X-ray diffractometer using $CuK_\alpha$ radiation and Cu/Ni filter. Crystal structure was determined from XRD data. Curie temperature measurements were performed by using impedance analyzer, with a laboratory built oven and a thermocouple based thermometer. Frequency dependence of complex initial permeability of the toroid-shaped samples was measured with the impedance analyzer. *BH* loops were measured by using BH Loop Tracer.

## 3. Results and discussion

### 3.1. XRD analysis

Fig. 1(a) shows X-ray diffraction patterns of $Li_{0.5-x/2}Cu_xFe_{2.5-x/2}O_4$ samples sintered at 1000 °C. It can be observed that the samples in the range of $0 \le x \le 0.3$ are cubic spinel. Tetragonality begins from the composition of $x=0.4$–0.8, which has been manifested by twin peaks in the XRD patterns. For the composition of $x=0.9$ and 1.0 presented in Fig. 1(b), it was found that tetragonality almost disappeared at 1000 °C. To study the variation of tetragonality with sintering temperature, these two samples were sintered at 1100 and 800 °C. For the sintering temperature of 800 °C, both $x=0.9$ and 1.0 showed ideal tetragonal structure, which has been presented in Fig. 1(b). At the sintering temperature of 1100 °C, the samples again exhibited cubic spinel structure. It is known that tetragonality is very much dependent on sintering temperature and concentration of copper. At 1100 and 1200 °C, X-ray diffraction pattern reveals transformation to cubic structure for all compositions up to $x=1.0$. Though existence of tetragonal deformation has later been found from temperature dependence of initial permeability and other results for much lower content of Cu, this is not detectable in XRD patterns.

Composition dependence of lattice parameters was determined for the sintering temperatures of 1100 and 1200 °C by using Nelson–Riley extrapolation, which can be expressed by $F(\theta)=(1/2)[(\cos^2\theta/\sin\theta)+(\cos^2\theta/\theta)]$, where $\theta$ is Bragg's angle [12,13] and presented in Fig. 2. From Fig. 2, it is observed that the lattice parameter increases with the increase in Cu content. This behavior can be attributed to the replacement of $Fe^{3+}$ (0.64 Å) and $Li^+$ (0.68 Å) by $Cu^{2+}$ (0.72 Å) ion [14]. The lattice parameter of Li–Cu ferrite system with composition has been significantly deviated from Vegard's law [15] because of the cubic to tetragonal deformation at higher Cu content. It may be noticed from Fig. 2 that the deviation is more for the sintering temperature of 1100 °C than for 1200 °C. This is because for the lower sintering temperature tetragonal deformation is more. This deformation has gradually been eliminated and transformed into more cubic symmetry as the sintering temperature rises. However, even for the sintering temperature of 1200 °C, deviation from linear variation of lattice parameter with composition is again significant for higher Cu content.

The bulk densities were calculated from $\rho_B=M/V$ and X-ray densities calculated from $\rho_{X\text{-ray}}=8M_A/N_Aa^3$, respectively, where $M$ is the mass of the sample, $V$ the volume, $M_A$ the molecular weight, $N_A$ Avogadro's number and $a$ the lattice parameter. The variation in X-ray and bulk densities as a function of Cu content has been presented in Fig. 3 for the samples sintered at 1100 °C. It is clearly seen that both densities increase with the increase in Cu content.

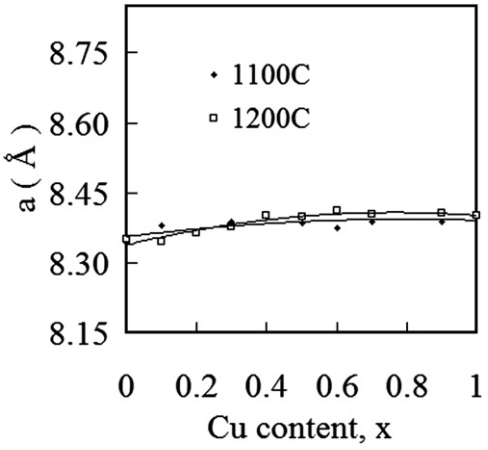


**Fig. 2.** Variation of lattice parameters with Cu content, sintered at 1100 and 1200 °C.

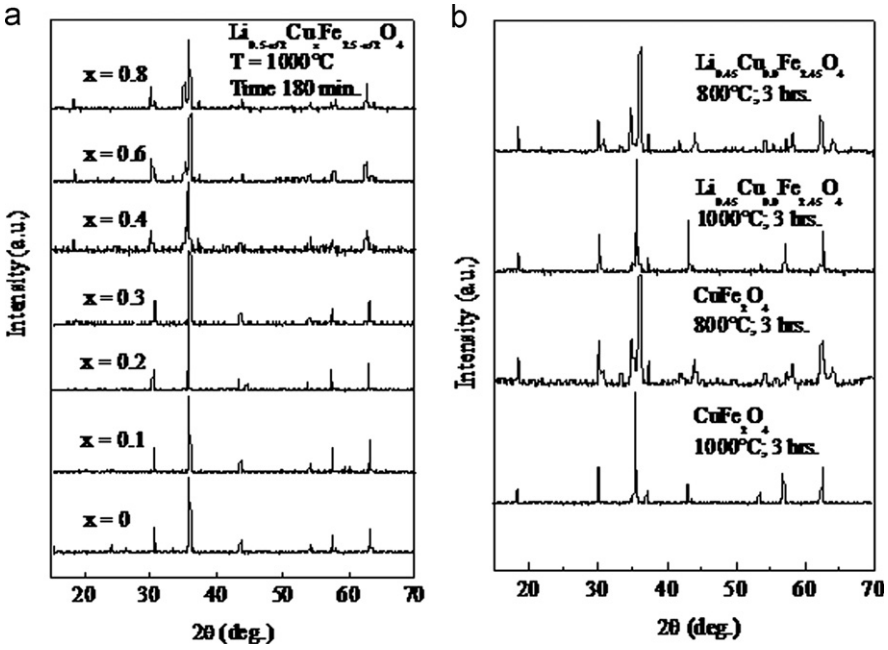


**Fig. 1.** XRD patterns of $Li_{0.5-x/2}Cu_xFe_{2.5-x/2}O_4$ ferrites.