

Preparation and Structural Properties of Aluminium Substituted Lithium Nano Ferrites by Citrate-Gel Auto Combustion method

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Abstract: Nano sized particles of aluminium doped lithium nano ferrites having general formula $Li_{0.5}Al_xFe_{2.5-x}O_4$ (where $x=0.0,0.2,0.4,0.6,0.8,1.0$) were prepared by the citrate gel method at low temperature ($180^\circ C$). The synthesized powders were sintered at $500^\circ C$ for 4 hours. The crystal structure characterization of the sintered powders were carried out by using X-ray diffraction (XRD). The X-Ray diffraction analysis confirmed the formation of single phase cubic spinel structure. The average particle size of the synthesized powders was 13 to 27 nm. The surface morphology were studied by Scanning Electron Microscopy (SEM) which revealed the formation of largely agglomerated nano particles. Lattice parameter, X-ray density, experimental density, porosity of the samples were calculated. The observed results can be discussed in this paper on the basis of composition.

Keywords: citrate gel method; lithium nano ferrites; Scanning Electron Microscopy; surface morphology

I. Introduction:

The study of nanoferrites has attracted immense attention of the scientific community because of their novel properties and technological applications especially when the size of the particle approaches to the nanometer scale. More novel electrical and magnetic behavior have been observed in comparison with their bulk counterpart.[1-2]. In general, the transport properties of the nano materials are predominantly controlled by the grain boundaries than by the grain itself[3]. Due to this reason, the magnetic materials have explored a wide range of applications and thus are replacing conventional methods.

Commonly used ferrites are primarily classified into three types: spinels, hexagonal ferrites, and garnets according to their primary crystal lattice. Generally, ferrimagnetism arises from the antiparallel alignment of the magnetic moments on transition metal ions, present on different magnetic sublattices. The origin of the antiparallel coupling can be explained by super-exchange of valence electrons between the filled p-orbitals of O^{2-} and unfilled d-orbitals of the transition metal cations.

Spinel ferrites have the general formula $MO.Fe_2O_3$ where M represents a divalent transition ion or a combination of ions having an average valence of two. The crystal structure of a ferrite can be regarded as an interlocking network of positively charged metal ions and negatively charged divalent oxygen ions. In spinel ferrites, the relatively large oxygen anions form a cubic close packing with $\frac{1}{2}$ of the octahedral and $\frac{1}{8}$ of the tetrahedral interstitial sites occupied by metal ions.

Lithium ferrite has been a widely investigated material due to its impotence in construction and engineering of many electromagnetic and microwave devices[4-6]. Bulk lithium ferrite has an inverse cation distribution of the form $(Fe^{3+})_A[Li_{0.5}Fe_{1.5}]_B$. The interplay between the superexchange interactions of Fe^{+3} ions at A and B sublattices gives rise to ferri magnetic ordering of magnetic moments[7,8]. Ease of fabrication, low cost, high Curie temperature and better temperature stability of saturation magnetization of lithium ferrites have made them attractive from commercial point of view and are good substitutes of garnets for microwave devices such as isolators, circulators, gyrators, and phase shifters. Lithium ferrite has an important role in microwave latching devices, magnetic switching circuits and can also be used as cathode material in lithium batteries. There are many reports on the effect of magnetic and non-magnetic substitutions on various properties of lithium ferrite[9-12].

Nano ferrites were usually prepared by the conventional ceramic methods but the resultant products are not necessarily always stoichiometric or homogeneous[13]. A variety of chemical synthesis methods such as coprecipitation, hydrothermal synthesis, and sol-gel process have been developed.[14-16]. The Citrate-gel auto combustion technique has been used for the preparation of mixed nano crystalline spinel ferrites with specific properties, such as controlled stoichiometry and narrow particle size distribution. The low cost, simplicity and short time of production and the purity and homogeneity of final product are included among its advantages[17].

II. Experimental Details:

The Aluminium substituted lithium nano ferrite particles having the general formula

$Li_{0.5}Al_xFe_{2.5-x}O_4$ (where $x=0.0,0.2,0.4,0.6,0.8,1.0$) were synthesized by citrate-gel auto combustion technique at a very low temperature ($180^\circ C$) using the below mentioned raw materials.

2.1 Raw Materials:

- *Lithium Nitrate-99% Pure (AR Grade) (LiNO₃)
- * Aluminum Nitrate -99% Pure (AR Grade)Al(NO₃)₃.9H₂O
- *Ferric Nitrate-99% pure(AR grade) (Fe(NO₃)₂9H₂O)
- *Citric acid - 99% pure (AR grade) (C₆H₈O₇.H₂O) .
- *Ammonia - 99% pure (AR grade) (NH₃)

2.2.Synthesis:

Required quantities of metal nitrates were dissolved in a minimum quantity of distilled water and mixed together. Aqueous solution of Citric acid was then added to the mixed metal nitrate solution. Ammonia solution was then added with constant stirring to maintain P^H of the solution at 7. The resulting solution was continuously heated on the hot plate at 100°C up to dryness with continuous stirring. A viscous gel has resulted. Increasing the temperature up to 200°C lead the ignition of gel. The dried gel burnt completely in a self propagating combustion manner to form a loose powder. The burnt powder was ground in Agate Mortar and Pestle to get a fine ferrite powder. Finally the burnt powder was calcinated in air at 500°C temperature for four hours and cooled to room temperature.

2.3. XRD Analysis: Structural characterization of the prepared samples were carried out using X-ray Diffraction with CuK_α radiation of wavelength 1.5405Å. Using these we study the single phase nature and nano-phase formation of the Li-Al ferrite system at room temperature by continuous scanning in the range of 10° to 80° in steps of 0.04°/Sec.

The crystalline size was calculated for all the samples using the high intensity peak and using the Debye Scherrer formula [18] while taking into account the intensity broadening[19]. The Debye Scherrer formula assumes approximations and gives the average grain size if the grain size distribution is narrow and strain induced effects are small.

Scherrer Formula:

$$\text{Crystallinesizeofthesample } D = \frac{0.91\lambda}{\beta \cos\theta}$$

Where λ is the wavelength of X-ray used [20]

β is the Width of diffraction peak i.e.

Full Width Half Maxima(FWHM) in radians.

θ is the peak position.

Lattice parameter(a) of the sample was calculated by the formula

$$a = d * (h^2 + k^2 + l^2)^{1/2} [20]$$

Where a= Lattice Constant

(hkl) are the Miller Indices

d is the inter planner spacing,

The X-ray density of the prepared sample was calculated using the relation

$$d_x = \frac{nM}{a^3 N} [g/cm^3] [21]$$

Whwre M = molecular weight of the sample

n is the number of molecules in a unit cell of spinel lattice.

a is the lattice parameter and N is the Avogadro number.

The Volume of the Unit Cell V= a³

The experimental density of the prepared sample was calculated by Archimedes’s principle with xylene media using following relation.

$$d_E = \frac{\text{Weight of the sample in air}}{\text{Weight of the sample in air} - \text{Weight of the sample in xylene}} \times \text{Density of Xylene}$$

The Percentage of Porosity P of the ferrite sample was then determined by employing the relation

$$P = \frac{d_x - d_E}{d_x} \times 100$$

Where d_x is the X-ray density & d_E is the experimental density.

The distance between the magnetic ions (hoping length) on A-site(Tetrahedral) and B site(Octahedral) is calculated according to the following relations

$$d_A = 0.25a\sqrt{3} \text{ and } d_B = 0.25a\sqrt{2} [22]$$

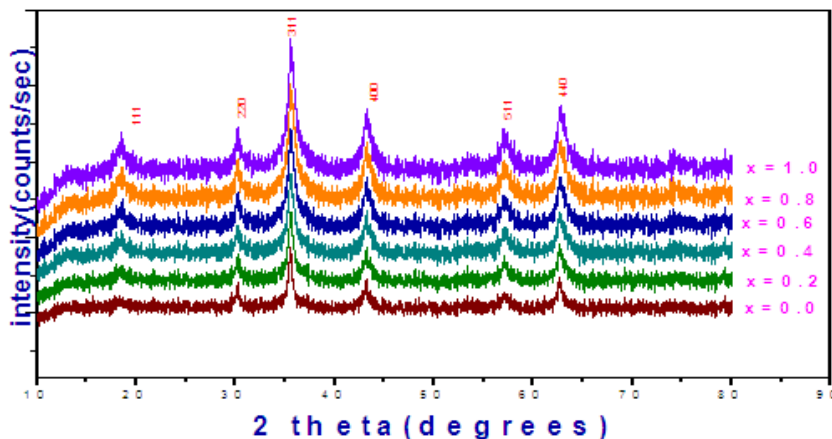
Where ‘a’ is the lattice parameter

2.4SEM Studies:

Micro structural analysis (surface morphology)of the prepared samples was carried out by scanning Electron microscopy (SEM).

III. Results and Discussions:

The X-ray diffraction pattern of the Aluminum substituted lithium nano ferrites were shown in fig(1). It can be seen from the figure all Bragg's reflections have been indexed, which confirm the formation of cubic spinel structure in single phase without any impurity peak. The strongest reflection comes from the (311) plane, which denotes the spinel phase. The peaks indexed to (220)(311)(400)(422)(511) and (410) of a cubic uni cell, all planes are the allowed planes which indicates the formation of cubic spinel structure in single phase.



Fig(1): XRD Pattern of Li-Al Nano ferrites

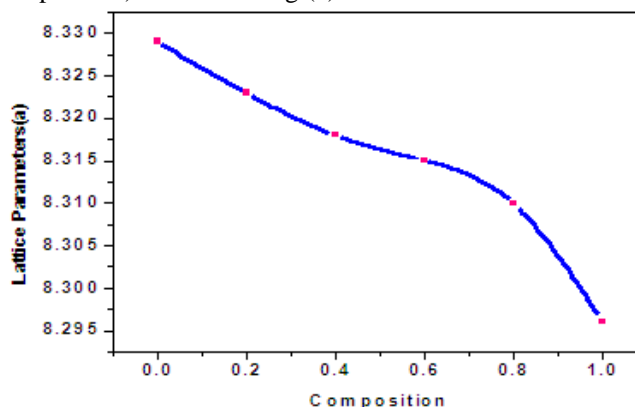
The calculated values of crystalline size for the different compositions are given in the table(1).

It can be seen from the table that the values of the crystal size varies from 13nm to 27nm. The crystalline size was not same for all Al concentrations because the preparation condition followed here which gave rise to different rate of ferrite formation for different concentrations of Al, favoring the variation of crystalline size. Conventional methods needs to high temperatures and more time, but in this method, ferrite phase can be produced very fast at low temperature.

Table (1). Values of the Crystalline size, Lattice parameter(a), X-ray density(d_x), Experimental density(d_E) and Porosity.

Sl.No	Composition	Molecular weight	Particle size(D) nm	Lattice parameterA°	X-ray Density gm/cc	Expt Density gm/cc	Porosity (%)
1	$Li_{0.5}Fe_{2.5}O_4$	207.091	27.31	8.329	4.760	4.388	7.8
2	$Li_{0.5}Al_{0.2}Fe_{2.3}O_4$	201.317	24.82	8.323	4.637	4.206	9.2
3	$Li_{0.5}Al_{0.4}Fe_{2.1}O_4$	195.543	17.69	8.318	4.548	4.138	9.0
4	$Li_{0.5}Al_{0.6}Fe_{1.9}O_4$	189.770	18.71	8.315	4.414	4.074	7.7
5	$Li_{0.5}Al_{0.8}Fe_{1.7}O_4$	183.996	15.98	8.310	4.264	3.976	6.7
6	$Li_{0.5}Al_{1.0}Fe_{1.5}O_4$	178.223	13.74	8.296	4.146	3.835	7.5

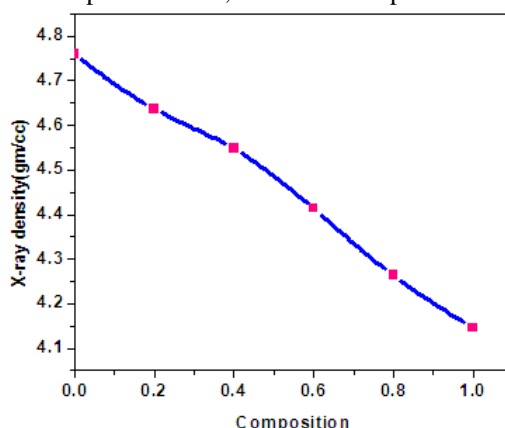
The lattice parameter values of all the compositions of aluminum doped lithium nano ferrites have been calculated from the d-spacing and are given in the above table. A plot is drawn between the lattice parameter vs Aluminum ionic content (composition) is shown in fig (2).



Fig(2):Variation of Lattice Parameter vs Composition

The decrease in the lattice parameter (a) is observed with increase in concentration of Al^{+3} in Li-ferrites as shown in fig(2), which obeys the Vegard's law[23]. The decrease in the lattice parameter with

increase of the Al^{+3} concentration can be explained on the basis of the relative ionic radii of the Al^{+3} and Fe^{+3} ions since radius of Al^{+3} (0.535\AA) is smaller than that of Fe^{+3} (0.645\AA) [24]. The substitution of smaller ions by larger ions results in the shrinkage of the lattice [25]. The decrease in the value of the lattice parameter when Fe is replaced by the Al, as observed in the present work, is therefore expected.



Fig(3): Variation of X-ray density with composition

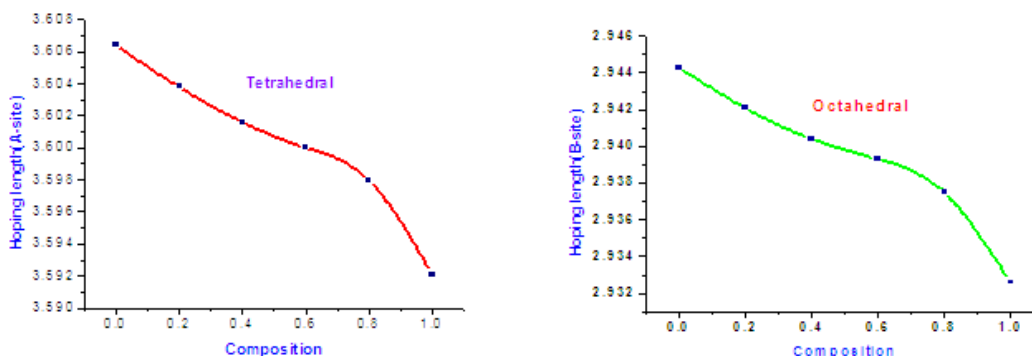
The values of the experimental density of all the samples (pellets) are determined by using Archimedes principle are given in table (1). From the table it can be observed that experimental density of the Al substituted Li ferrites was observed to decrease with Al concentration, while all the other experimental conditions were kept identical for these samples [26]. Enhanced densification of the samples are observed in the citrate gel prepared samples, this is one of the advantages of this preparation technique. The experimental density values are observed to be >85% of the densities evaluated from X-ray diffraction. The values are found to be in the range 3.835 to 4.388 gm/cc for Aluminum doped Lithium ferrites.

A graph is plotted between the X-ray density (d_x) vs Al concentration is shown in fig(3). From the graph one can observe that experimental density of the Al substituted Li ferrites was observed to decrease with Al concentration. The X-ray density (d_x) depends on the lattice parameter and molecular weight of the sample. From the table one can observe that molecular weight of the sample decreases with Aluminum concentration and lattice parameter is also decreased. This may be due to the greater atomic weight of Fe-55.85 gm/mol and lesser atomic weight of Al-26.98 gm/mol. [27]

Table(2): Values of the Volume(V), Hoping length of A-site and B-site:

S.No	Composition	Volume(\AA^3)	A-site(d_A)	B-site(d_B)
1	$Li_{0.5}Fe_{2.5}O_4$	577.801	3.6064	2.9443
2	$Li_{0.5}Al_{0.2}Fe_{2.3}O_4$	576.553	3.6038	2.9421
3	$Li_{0.5}Al_{0.4}Fe_{2.1}O_4$	575.515	3.6016	2.9404
4	$Li_{0.5}Al_{0.6}Fe_{1.9}O_4$	574.892	3.6000	2.9393
5	$Li_{0.5}Al_{0.8}Fe_{1.7}O_4$	573.856	3.5980	2.9375
6	$Li_{0.5}Al_{1.0}Fe_{1.5}O_4$	570.960	3.5921	2.9326

The calculated values of the Volume of the unit cell are tabulated in table(2). The Volume of the unit cell depends upon the lattice parameter. In the present case, the volume of unit cell of the Li-Al system decreases with increase of the Al concentration because lattice parameter decreases with increase of Al concentration.



Fig(4): Variation of Hopping Length with Composition

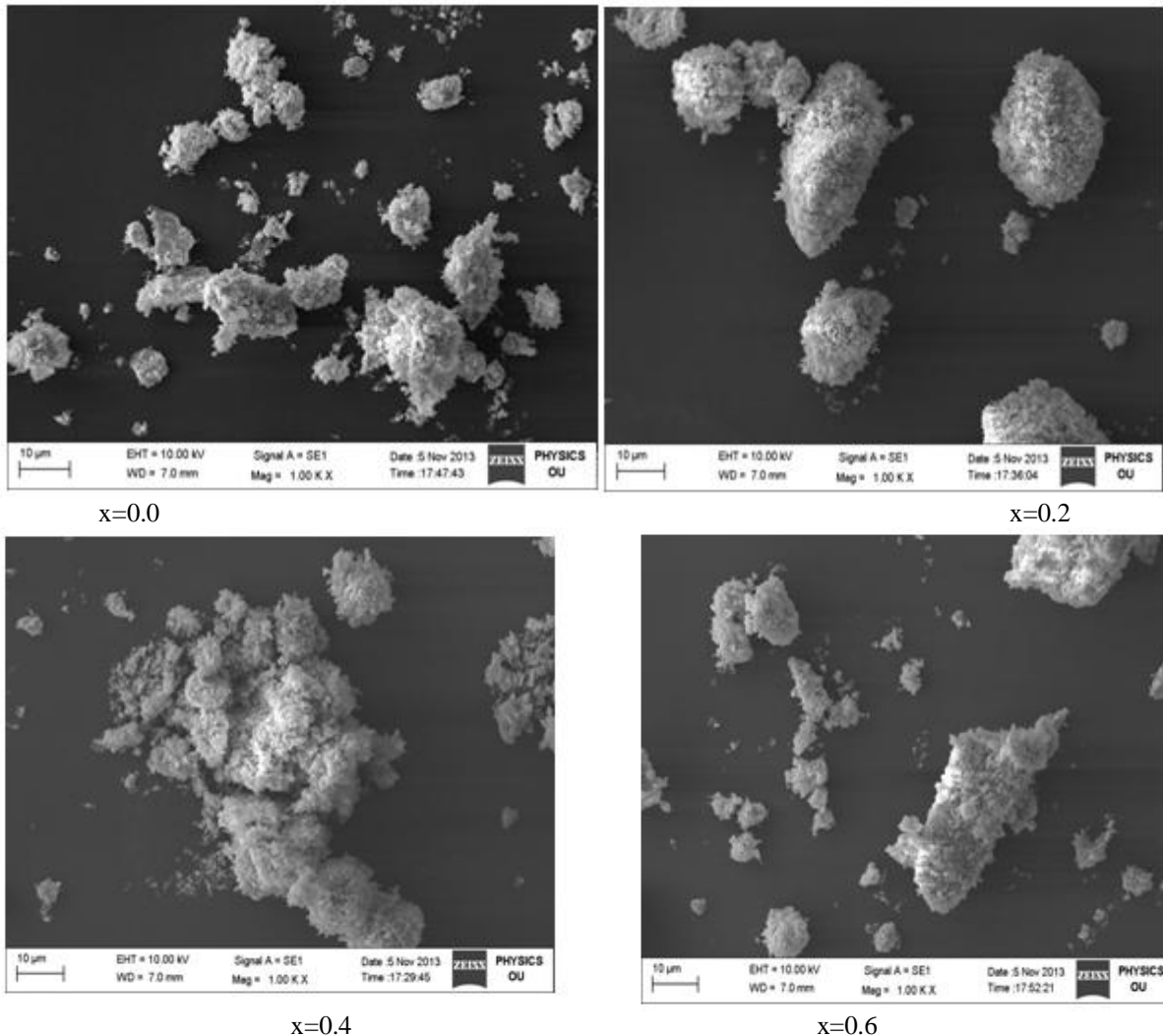
The values of the hopping length of the tetrahedral site(d_A) and Octahedral site (d_B) are calculated and tabulated in the table (2). A plot is drawn between the hopping length of the tetrahedral site(d_A) and Octahedral site(d_B) as a function of Aluminum concentration is shown in fig(4).

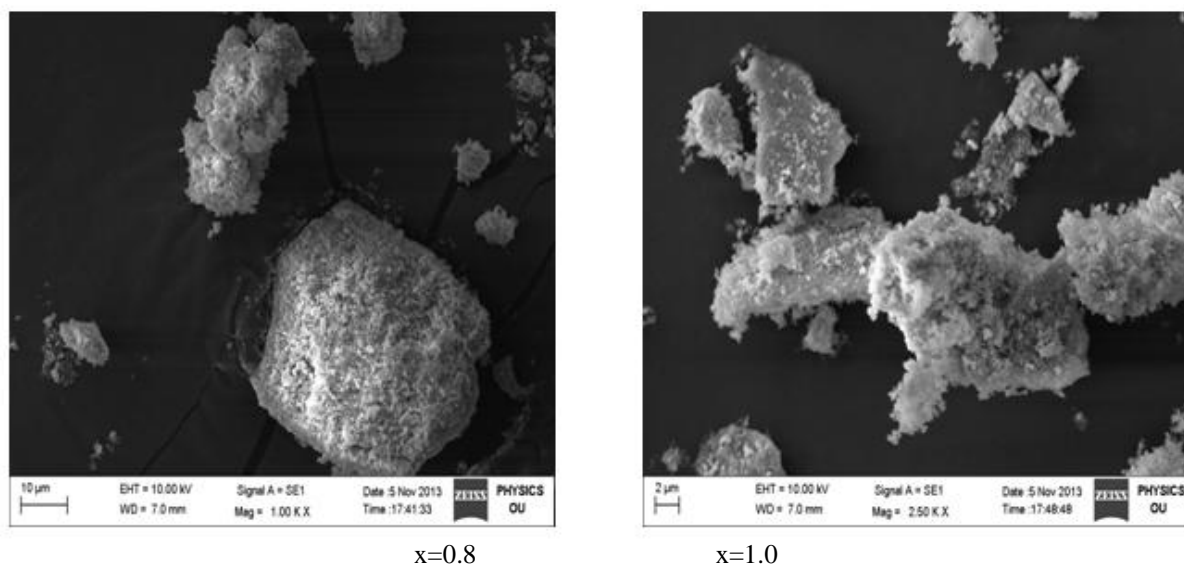
It is observed that the distance between the magnetic ions decreases with the increase of the Al content, because ionic radius of Al^{+3} ($53A^0$) is smaller than the Fe^{+3} ($64A^0$), which makes the magnetic ions closer to each other and hopping length decreases.

Surface Morphology by SEM:

The surface morphology of the sintered samples were studied using SEM(Scanning Electron Microscope). The secondary electron images are taken at different magnifications to study the morphology of samples by SEM. Fig(5) shows the SEM micro structures of the Aluminum doped Lithium nano ferrites.

The morphology and grain size of the samples seem to be non uniform with somewhat agglomeration in the synthesized samples which is unavoidable. From the preliminary observations of the SEM images, one can observe that the grain size is slightly affected by the Al doping concentration.





Fig(5). SEM micrographs of compositions of Li-Al Nano Ferrites

IV. Conclusions:

- The Citrate-Gel auto combustion method to be a convenient method for obtaining homogeneous mixed Li-Al nano ferrites without any impurity peak and material loss.
- X-ray diffraction pattern confirm that the formation of single phase cubic spinel structure. The crystalline size of the nano ferrites in the range 13-27nm.
- The lattice parameter is decreases with increase of Al composition in Li nano ferrites indicate that the mixed Li-Al nano ferrites obey Vegard's law.
- The distance between the magnetic ions on A and B calculated. It is clear that the distance between the magnetic ions decreases with increasing the Al content.
- SEM analysis explain that the morphology of the particle is similar and particle sharpness is more or less spherical with some cluster/ agglomeration between the particles.

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