

Cation Distribution in Lithium Ferrite (LiFe₅O₈) Prepared via Aerosol Route

Sonal Singhal^{1,*}, Kailash Chandra²

¹Department of Chemistry, Panjab University, Chandigarh, India; ²Institute Instrumentation Centre, Indian Institute of Technology, Roorkee, India.

Email: sonal1174@gmail.com, chandfuc@iitr.ernet.in

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ABSTRACT

Nano size lithium ferrite was prepared through aerosol route and characterized using TEM, XRD, magnetic measurements and Mössbauer spectroscopy. The particle size of as obtained samples were found to be ~10 nm through TEM, that increases upto ~80 nm on annealing at 1200 °C. The unit cell parameter 'a' calculated using XRD, confirms the formation of \mathbf{a} -LiFe₅O₈. Room temperature Mössbauer spectra of as obtained sample of all the ferrites exhibited broad doublet suggesting super paramagnetic nature. This doublet further resolved into two doublets and assigned to the surface region atoms and internal region atoms of the particles. The annealed samples (1200 °C) show broad sextets, which were fitted with two sextets indicating different local environment of both tetrahedrally and octahedrally coordinated Fe-cation. Cation distribution obtained from the X-ray, magnetic and Mössbauer data confirms that the three fifth of the iron atom goes in to the octahedral site.

Keywords: Nano Particles, Saturation Magnetization, Coercivity, X-Ray Diffraction, Mössbauer Spectra

1. Introduction

Lithium iron oxides LiFe₅O₈ are of increasing scientific interest and are also promising candidates for cathode materials in rechargeable lithium batteries [1,2]. Its high curie temperature, high saturation magnetization and hysterisis loop properties after performance advantages over other spinel ferrites used in microwave frequency and magnetic core applications [1–4]. Two separate crystallographic ordered and disordered forms of LiFe₅O₈have been isolated. A super structured form in which lithium and iron atoms are ordered is called α - LiFe₅O₈ and has a subgroup of Fd-3m with a primitive cubic unit cell (space group P4₃3 or P4₁3, a = 8.3372 Å) [5]. They are based on the inverse spinel structure with lithium and three fifth of the total Fe^{3+} occupying octahedral sites [6]. However, disordered form of lithium ferrites has a random statistical distribution of lithium and iron over all the octahedral positions [7]. Various preparation methods have been developed such as double sintering ceramic techniques, hydrothermal precipitate, hydrothermal ball milling and so on [8,9]. The high temperature used in all these techniques lower the magnetization due to the precipitation of α -Fe₂O₃ or the formation of Fe₃O₄[10].

The present work deals with the synthesis of nano particles of lithium ferrite via aerosol route at a temperature ~600 °C. This avoids the precipitation of α -Fe₂O₃ or Fe₃O₄. On the other hand in aerosol method particle size, degree of agglomeration, chemical homogeneity can be controlled with relative ease. Aerosol method has the potential of producing multicomponent materials and production of powder by this method is commercially viable [10,11].

The sample so prepared was characterized using transmission electron microscope (TEM), X-ray diffractometer (XRD), magnetic and Mössbauer spectrometer. This work is an attempt to investigate the cation distribution using XRD, magnetic and Mössbauer measurements.

2. Experimental

Nano particles of lithium ferrite (LiFe₅O₈) were prepared via aerosol route using a setup described in our earlier papers [12–14]. The desired proportions of lithium and iron nitrates were weighed and dissolved in water to prepare 5 x 10^{-2} M solutions. Air pressure, sample uptake and furnace temperature were maintained at 40 psi, 3-4 ml/min and ~600 °C respectively during preparation. The ferrite powder was deposited on the teflon coated pan.

The elemental analysis was carried out on an electron probe micro analyzer (EPMA) (JEOL, 8600 M) and atomic absorption spectrophotometer (AAS) (GBC, Avanta),



Figure 1. X-ray diffractographs of LiFe₅O₈ after annealing at various temperatures

while the particle morphology was examined by transmission electron microscope (TEM) (Philips, EM400). The X-ray diffraction (XRD) studies were carried on Xray spectrometer (Bruker AXS, D8 Advance) with FeK α radiation and magnetic measurements were made on a vibrating sample magnetometer (VSM) (155, PAR). Mössbauer spectra were recorded on a constant acceleration transducer driven Mössbauer spectrometer using ⁵⁷Co(Rh) source of 25 mCi initial activity. The spectrometer was calibrated using a natural iron foil as well as recrystallized sodium nitroprusside dihydrate (SNP) as standards.

3. Results and Discussion

Elemental analytical data for Li and Fe were obtained by EPMA. About 2 mm thick pellet was prepared, fixed on the sample holder and coated with the carbon to make them conducting. Elemental analysis was carried out at eight different points on each pellet with spot size of ~10 μ m dia and results were found to be consistent. The results were further verified by atomic absorption spectro-photometer.

3.1 Transmission Electron Microscope

The TEM micrograph of a very small amount of as obtained samples placed on the carbon grid shows spherical particles of ~100-300 nm size as reported in our earlier papers [13,14]. However, after agitating ultrasonically and taking the suspended particles on the carbon grid shows well separated particles of size ~10 nm. The micrographs for sample annealed at 1200 °C shows that the particle size increases with annealing temperature. It is widely believed that the net decrease in free energy of solid-solid and solid-vapour interface provides the necessary driving force for particle growth during annealing process [15].

3.2 X-Ray Diffractographs

The powder X-ray diffractographs of as obtained sample and that of annealed at various temperatures is given in Figure 1. The diffraction pattern of as obtained samples confirms the amorphous nature of the samples. Peaks start appearing and the lines become sharper as the annealing temperature increases due to the grain growth at higher temperatures. The crystallite size was calculated from the most intense peak (311) using Sherrer equation [16]. It is seen that the particle size increases upto ~80 nm as the annealing temperatures are raised to 1200 °C. The lattice parameters were calculated using Powley as well as Le Bail refinement methods (built in TOPAS V2.1 of BRUKER AXS) and found to be a = b = c =8.33103 Å and V = 578.22 Å³. The data confirm the presence of α -LiFe₅O₈ formation. Rietvald analysis of the annealed sample further confirms a single phase cubic spinel structure, α -LiFe₅O₈, as given in Figure 2.

X-ray diffraction intensity calculations were carried out using the formula suggested by Buerger [17]

$$I_{hkl} = |F_{hkl}|^2 PL_p$$

where, notations have their usual meanings. It is well known that, the intensity ratio of planes I(220)/I(400), I(220)/I(440) and I(400)/I(440) are considered to be sensitive to the cation distribution, therefore, these ratios were used in estimating cation distribution. Finally, the cation distribution is estimated from X-ray intensity calculations for the best fit cation distribution and found to be $[Fe_2]^{A}[LiFe_3]^{B}O_8$.

3.3 Magnetic Measurements

Magnetic hysteresis loops, at room temperature were recorded for the as obtained as well as annealed sample. Typical loops for as obtained LiFe_5O_8 and after annealing at 1200 °C are shown in Figure 3. The as obtained sam-



Figure 3. Hysterisis loop of lithium ferrite sample (a) as obtained and (b) after annealing at 1200

ple exhibits no hysteresis, which may be attributed to superparamagnetic relaxation as confirmed by XRD. The values of saturation magnetization and magnetron n_B (the saturation magnetization per formula unit in Bohr magnetron) at 300 K for the annealed sample were obtained from the hysterisis loop and found to be 66.92 emu/g and 4.99 respectively. According to Neel's two sublattice model of ferrimagnetism, the magnetic moment per formula unit (μ_B), $n_B^{N}(x)$ is expressed as:

$n_{\rm B}{}^{\rm N}({\rm x}) = M_{\rm B}({\rm x}) - M_{\rm A}({\rm x})$

where M_B and M_A are the B- and A- sublattice magnetic moment in μ_B respectively. The $n_B{}^N(x)$ value was calculated using the ionic magnetic moments of Fe^{3+} and Li^+ which are 5 μ_B and 0 μ_B respectively. The calculated value (5 μ_B) clearly indicates the inverse spinel structure with lithium and three fifth of the total Fe^{3+} occupying octahedral sites and two fifth occupying tetrahedral site.

3.4 Mössbauer Spectra

Figure 4 shows the typical Mössbauer spectra of LiFe₅O₈ at room temperature for the as obtained sample. The presence of broad doublet in this figure indicates the superparamagnetic nature of the sample. Since in the small particles (<10 nm) a substantial fraction of atoms resides on the surface, a different environment is experienced by them as compared to those inside the particle. Therefore, this broad doublet was fitted with two sets of doublets, one for atoms in the surface region ($\delta = 0.45$ mms⁻¹ and $\Delta E_Q = 1.02 \text{ mms}^{-1}$) and the other for those in the internal region ($\delta = 0.45$ mms⁻¹ and $\Delta E_0 = 0.60$ mms⁻¹) of the particles. Larger quadrupole splitting due to surface region atoms compared to internal region atoms can be attributed to the existence of a broader distribution of interatomic spacing and partly disordering in the surface region of the ultrafine particles. It is clear that the contri-



Figure 4. Mössbauer spectra of lithium ferrite (a) as obtained and (b) after annealing at 1200 0 C

bution of surface region atoms is 42 % of total area of the experiment spectrum. This is in agreement with the percentage (44 %) of the volume of surface region atoms to the total volume of the particle with an average grain size (8 nm) by Ma *et al.* [18].

The Mössbauer spectra recorded at 300 K after annealing at 1200 °C (Figure 4b) exhibit two normal zeeman split sextets due to the A-site Fe^{3+} ions and other due to B-site Fe^{3+} having hyperfine fields 500 and 484 kOe respectively, which indicates ferrimagnetic behaviour of the sample. The cation distribution was also calculated using the intensity ratio of the sextets corresponding to the tetrahedral and octahedral sites. The intensity ratio was found to be 2 : 3 which further confirms that the three fifth iron atoms goes in to octahedral site. The cation distribution obtained from the X-ray intensity data and magnetic moment data agrees fairly well with the cation distribution estimated from Mössbauer data.

4. Conclusions

Lithium ferrite has been prepared successfully with particle size ~10 nm by aerosol route with high yield. After annealing the sample at 1200 °C confirms the formation of single phase α -LiFe₅O₈. The cation distribution obtained from the X-ray, magnetic and Mössbauer data confirms that the three fifth of the iron atom goes in to the octahedral site. Since Lithium ferrite and mixed lithium ferrites have very high potential for cathode materials in rechargeable lithium batteries, microwave applications and, especially as replacements for garnets, due to their low cost. The squareness of the hysteresis loop and superior temperature performance are other prominent advantages that have made them very promising candidates for application in microwave devices. In this communication we report our studies on the synthesis of lithium ferrite and their magnetic properties and the work is going on with the mixed lithium ferrites to improve their magnetic properties and their applications in different fields.

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