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Rietveld Refinement of Nanocrystalline $LiFeO_2$ Synthesized by Sol-Gel Method and Its Structural and Magnetic Properties

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ABSTRACT

Nanocrystalline lithium iron oxide $LiFeO_2$ was synthesized using sol-gel method. Rietveld analysis was performed to confirm the different phases associated in the formation of $LiFeO_2$. Quantitative Rietveld refinement revealed that sample contains: 39.9 wt% of cubic α-$LiFeO_2$ phase, 58.5 wt% of monoclinic β-$LiFeO_2$ and tetragonal 1.7 wt% of γ-$LiFeO_2$. The nanocrystalline nature of the prepared samples was confirmed by SEM analysis. The magnetic properties of $LiFeO_2$ showed ferromagnetic property at room temperature.

Keywords: Nanoparticles; $LiFeO_2$; Structural and Magnetic Properties

1. Introduction

Lithium iron oxide was found to be the most promising and very interesting materials due to their potential applications as a cathode for rechargeable lithium batteries and also due to low cost and toxicity [1-3]. Lithium iron oxide $LiFeO_2$ has NaCl type cubic closed packed (ccp) crystal structure with Li^+ and Fe^{3+} being distributed in octahedral sites. $LiFeO_2$ crystallizes in different polymorphic modifications (α, β, γ) based on the synthesis techniques and preparation conditions [4-6]. The unit cell of α-$LiFeO_2$ has cubic distorted form with space group Fm3m. In α-$LiFeO_2$ structure, Li^+ and Fe^{3+} ions occupy randomly the octahedral sites [7]. γ-$LiFeO_2$ structure is tetragonal cation disordered. Li^+ and Fe^{3+} in the octahedral sites transform from cubic structure (Fm3m) to tetragonal (I4/m) structure [8]. In the case of monoclinic β-$LiFeO_2$ the cation ordering was detected [5,8]. It was observed that synthesis of $LiFeO_2$ is a difficult task as several phases are associated during preparation process. Earlier $LiFeO_2$ have been synthesized by different techniques such as hydrothermal [6,9], citrate precursor method [10], solid state reaction [11], ion exchange reaction [12] etc. and observed different polymorphic phases and improved structural and electrical properties. In this paper we made an attempt to synthesize nanocrystalline $LiFeO_2$ using sol-gel method. To clearly understand the structural formation and the corresponding phases of $LiFeO_2$ and the underlying magnetic properties we have carried the present work.

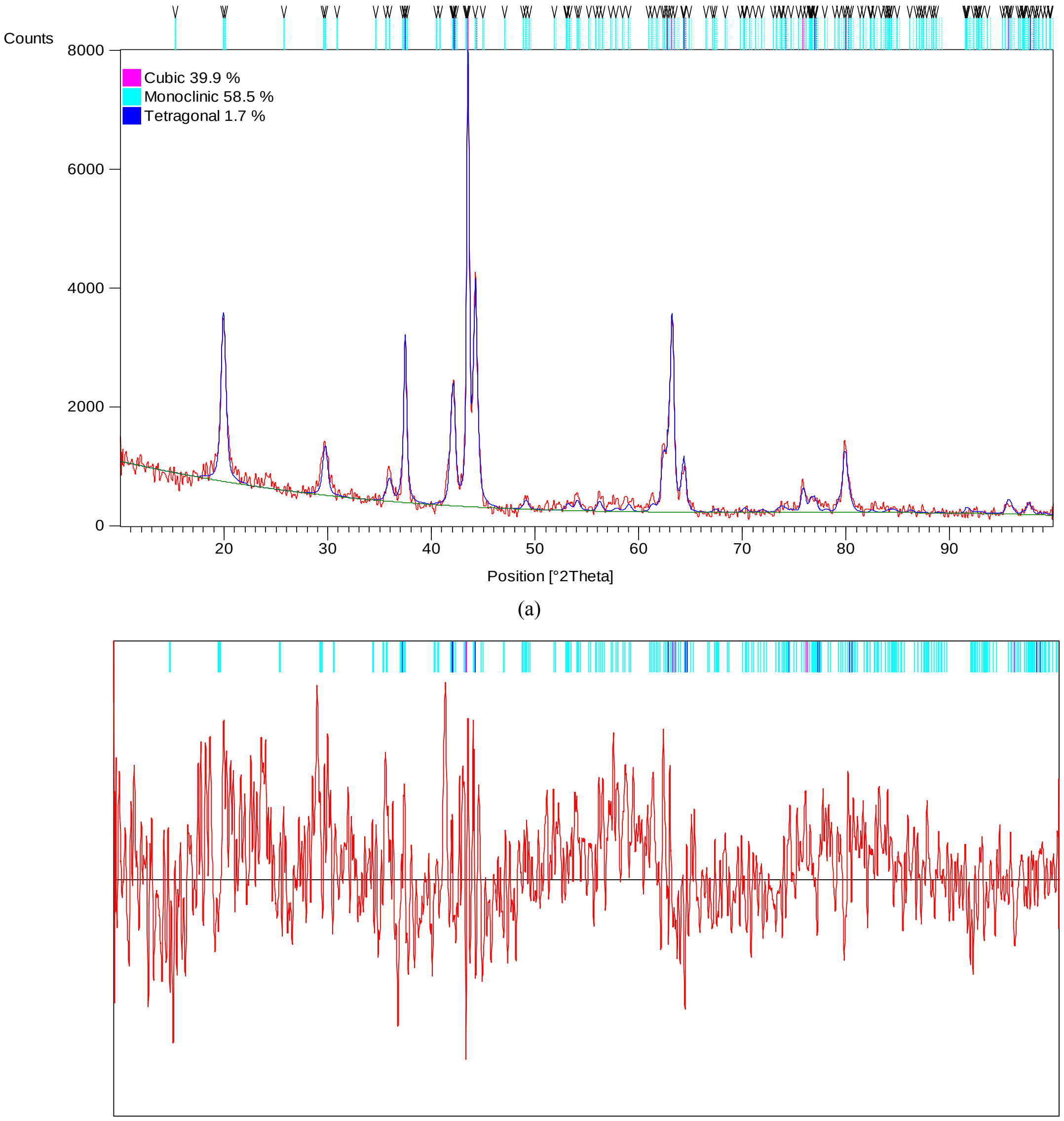
2. Experimental

The $LiFeO_2$ nanoparticles have been synthesized by sol-gel method [13]. The AR grade citric acid ($C_6H_8O_7{\cdot}H_2O$), ferric nitrate ($Fe(NO_3)_3{\cdot}9H_2O$) and lithium nitrate ($LiNO_3$) (≥99%) were used as starting materials. The entire synthesis procedure is described elsewhere [13]. The as prepared powder samples were sintered at 500˚C for 5 h.

Crystallographic structure of $LiFeO_2$ nanopowder was measured using Philips PW 3020 Bragg-Brentano diffractometer using Cu Kα radiation (wave length $\lambda = 1.54$ Å). The morphology of powder was observed using scanning electron microscopy (SEM) from Carl Zeiss. Room temperature magnetization was measured using ADE magnetics DMS 4 Vibrating Sample Magnetometer (VSM).

3. Results and Discussions

Figure 1 shows (a) experimental and (b) calculated X-ray diffraction patterns of nanocrystalline $LiFeO_2$. Crystal structures of different phases present in the



(a)

(b)

Figure 1. Rietveld analysis of nanocrystalline $LiFeO_2$ (a) experimental and (b) calculated data.

sample were refined by the Rietveld method. The analysis started using the structural models from the Inorganic Crystal Structure Database (2011) as follows: card No. 174084-ICSD, 28366-ICSD, 28364-ICSD for $LiFeO_2$ monoclinic, tetragonal and cubic structures. Rietveld structure refinement was performed with the program X'Pert High Score Plus (PANalytical 2009) using a pseudo-Voigt profile function and polynomial background model. During the Rietveld analysis, the following parameters were refined: profile parameters W and V, asymmetry parameter 1 and peak shape parameter 1, as well as the atomic fractional coordinates. Isotropic displacement parameters were assumed for all atoms. The preferred-orientation correction did not significantly improve the fit. Refinement converged with Rwp 9.8% which indicates a good reliability of the result. Refined unit-cell parameters for both phases were as follows:

1) Crystal structure—Monoclinic (β-Phase, 174084 ICSD), space group C12/c1 (15), lattice parameters a = 5.795(3) Å, b = 11.580 (5) Å, c = 5.157 (2) Å.

2) Crystal structure—Tetragonal (γ-Phase, 28366 ICSD), space group I4/m (87), lattice parameters a = 2.8926 (9) Å, c = 4.283 (2) Å.

3) Crystal structure—Cubic (α-Phase, 28364 ICSD), space group Fm3m (225), lattice parameters a = 4.1585 (8) Å.

Quantitative Rietveld refinement revealed that sample contains: 39.9 wt% of cubic α-$LiFeO_2$ phase, 58.5 wt% of monoclinic β-$LiFeO_2$ and tetragonal 1.7 wt% of γ-$LiFeO_2$.

The morphology of nanocrystalline $LiFeO_2$ as observed from SEM is shown in **Figure 2**. The morphology shows the un-even particle size distribution with an average particle size of 100 nm.

$LiFeO_2$ powder showed spontaneous magnetization at room temperature as shown in **Figure 3**. The magnetization curve clearly shows the ferromagnetic behavior having the maximum magnetization value 0.2 emu/g and coercivity of 189 Oe. The magnetization curve does not seem to be saturated even with the maximum applied field of 20 kOe. The observed magnetization value is very small compared to $LiFeO_2$ prepared using different techniques. The lower magnetization value in our nanocrystalline $LiFeO_2$ may be probably due to the occurrence of different phases in the synthesized sample. Tabuchi *et al.* [8,14] showed that the individual α, β, γ $LiFeO_2$ phases behave paramagnetic at low temperature and ferromagnetic at room temperature. Ferromagnetic impurities such as $LiFe_5O_8$ could influence the magnetic properties of $LiFeO_2$. It was observed that $LiFeO_2$ is antiferromagnetic below 90 - 280 K [15,16]. But in our samples we could not see any ferromagnetic impurities. The ferromagnetism observed for our samples may be due to the presence of different phases in our $LiFeO_2$. For a single phase $LiFeO_2$ it is expected to show higher magnetization value, where as for multiple phases in $LiFeO_2$ could lower the magnetization values.

4. Conclusion

Nanocrystalline lithium iron oxide $LiFeO_2$ was synthesized using sol-gel method. Rietveld analysis showed the different phases corresponding to α—cubic, β—monoclinic and γ—tetragonal polymorphic $LiFeO_2$ phases. SEM analysis showed the nanocrystallinity with particle size of 100 nm. The synthesized sample showed ferromagnetic property at room temperature.

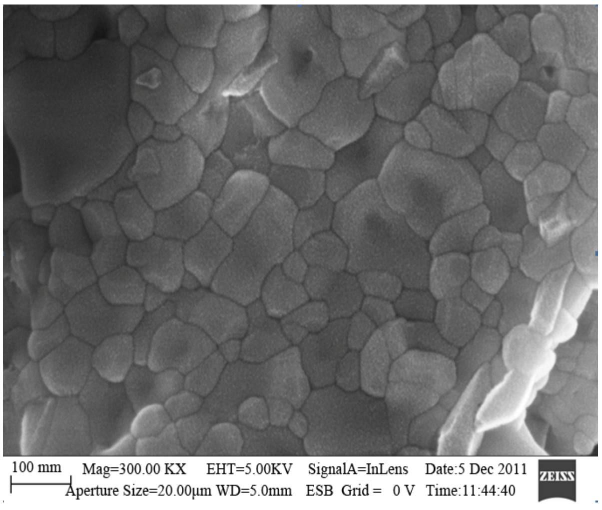


Figure 2. SEM image of nanocrystalline $LiFeO_2$.

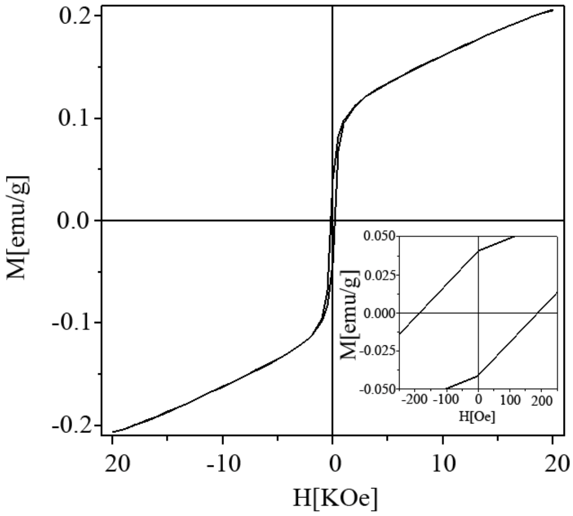


Figure 3. M-H curve of nanocrystalline $LiFeO_2$, measured at 300 K. Inset shows the expanded field curve.

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