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Ce-substituted Lithium Ferrite: Preparation and Electrical Relaxation Studies

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Ce-substituted lithium ferrite, $Li_{0.5}Ce_xFe_{2.5-x}O_4$ ($x = 0$, 0.05 and 0.1) compositions were synthesized from metal nitrates and citric acid by the solution combustion process by keeping the oxidizer to fuel ratio at unity. The thermal decomposition process was investigated by thermogravimetry−differential thermal analysis, which showed a stable phase formation above 600 °C. The phase composition and molecular bonding of $Li_{0.5}Ce_xFe_{2.5-x}O_4$ were characterized by X-ray powder diffraction analysis and Fourier transform infrared spectroscopy, respectively. An extensive study of electrical relaxation process has been represented with impedance and modulus as a function of frequency at different temperatures. The activation energy obtained from both the formalisms was found to be equal within the error. The dc conductivity and hopping frequency were thermally activated and their activation energies were found to be in the range of 0.69−0.64 eV for $x = 0.05$. The scaling of modulus and impedance were used to understand the electrical relaxation behaviour of the compositions and they suggest the time temperature superposition principle.

KEY WORDS: Lithium ferrite; Solution combustion synthesis; Inverse spinel; Electrical relaxation process and scaling

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1. Introduction

The field of ferrites is very significant due to their various potential applications and interesting physics involved in it. Among the ferrites, Inverse spinel lithium ferrite $Li_{0.5}Fe_{2.5}O_4$ has drawn the attention from a long time due to its prolonged applications in various microwave devices and memory core systems[1]. Along with high Curie temperature, square loop properties, high saturation magnetisation, thermal stability and safety of lithium ferrite make this material suitable for application in Li-ion batteries as a cathode material[2,3]. Recently, a lot of progress has been seen to understand various physical phenomena involved in mixed ferrites, particularly in mixed lithium ferrites[4−9]. It has been reported that properties such as thermal and electrical conductivity and electromagnetic behaviour could be enhanced by substituting them with rare earth elements[10] like La^{3+}, Gd^{3+}, Nd^{3+} etc. The lithium ferrite spinel contains reducible iron ions and lithium ions and therefore, it is expected that this material exhibit both electronic and ionic conductivities.

Solution combustion technique is a versatile method for preparation of nano-crystalline materials at low temperature with a single pure phase[11]. In the present work, we have focused on the preparation and electrical relaxation studies of Ce-substituted lithium ferrite by the solution combustion technique. Literature survey has confirmed that there is no information available on the synthesis, characterization and electrical properties of inverse spinel type Ce-substituted lithium ferrite systems. Recently some workers have reported about the microwave and dielectric properties of the Ce-substituted lithium ferrite[12,13]. The phase composition and microstructure of $Li_{0.5}Ce_xFe_{2.5-x}O_4$ were characterized by X-ray diffraction (XRD) analysis and Fourier transform infrared spectroscopy (FTIR). A thorough study on electrical properties has been reported in terms of impedance and modulus. Since there is no dispersive feature below 200 °C in the frequency window of 10^2−10^7 Hz, the electrical properties has been reported in terms of impedance and modulus in the temperature range of 473−573 K only. The results so obtained have been discussed and the various conclusions drawn have also been presented.

2. Experimental

Self propagating, simple and cost effective solution combustion process is a potential technique for preparation of a variety of phase pure nano-crystalline materials. This method provides an easy alternative for the preparation of nano-crystalline materials at low temperature and in a short time, i.e. homogeneous single phase can be obtained at low temperature[11].

According to stoichiometric composition of $Li_{0.5}Ce_xFe_{2.5-x}O_4$ (x = 0.0, 0.05 and 0.1), specified molar amount of nitrates $LiNO_3$, $Fe(NO_3)_3 \cdot 9H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ were dissolved in a citric acid aqueous solution under stirring. In the present case,

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fuel (F) to oxidizer (O) ratio is maintained unity i.e. $1 = O/(-n)$ F, where n is molar fraction of fuel, in order to maximize the energy released during the combustion process[14−16]. Here, all metal nitrates act as oxidizing agent and the fuel citric acid as a reducing agent for the combustion reaction. Hence, the stoichiometric composition of the redox mixture requires $n = 2.2$ mol of citric acid[17]. After a homogeneous transparent solution was achieved within few minutes, an appropriate amount of ammonia hydroxide solution was added to the solution to adjust the pH value to about 8 to avoid precipitate formation. After the formation of viscous liquid, it was kept in a heating mantel and evaporated to produce sample in powder form. The overall reaction for the sample is:

$$\begin{aligned}&0.5\mathrm{LiNO_3} + x\mathrm{Ce(NO_3)_3\cdot 6H_2O} + (2.5-x)\mathrm{Fe(NO_3)_3\cdot 9H_2O}\\ &\quad + n\mathrm{C_6H_8O_7} \xrightarrow{\Delta} \mathrm{Li_{0.5}Ce_xFe_{2.5-x}O_4} + 4\mathrm{N_2} + 6n\mathrm{CO_2}\\ &\quad + (22.5+4n-3x)\mathrm{H_2O} + (10-4.5n)\mathrm{O_2} \qquad (1)\end{aligned}$$

The thermal decomposition processes of the powder were characterized using thermogravimetry−differential thermal analysis (TG−DTA) instrument (Model: Q600 SDT) from TA instruments under nitrogen flow. The XRD patterns of 900 °C sintered pellets were obtained for the sample using X'pert PANalytical X-ray diffractometer with monochromatic Cu-$K\alpha$ radiation at glancing angles in the range of 2θ from 10° to 80° in a step size of 0.02°. FTIR were recorded using Thermo Nicolet made spectrometer (Model: 6700). The spectrum was recorded between 400 $\mathrm{cm^{-1}}$ and 1300 $\mathrm{cm^{-1}}$ using KBr as the diluting agent. Before carrying the electrical measurements, the pellets were sintered at 900 °C for 12 h. The densities of the compositions were measured by Archimedes principle and the parallel and opposite sides of the pellets were painted with silver paint. The electrical properties were measured using a Material Mates Impedance Analyzer 7260, in the temperature range of 473−623 K, measuring the real and the imaginary part of the sample impedance in the frequency range of 10^2−10^7 Hz.

3. Results and Discussion

3.1. TGA

The samples by autocatalytic combustion process of the prepared sample were investigated by thermal gravimetric analysis (TGA). Fig. 1 shows the TGA result conducted on the powder of prepared samples for $x = 0.0$. From the analysis of TG data, three obvious mass losses were observed with a total weight loss of 23%. An extremely weak mass loss of around 3% is observed before 100 °C due to the evaporation of water vapours. In the second step of weight loss, the weight loss is around 10% ascribed to the decomposition of organic fuel/complexing agent and nitrates at 250−580 °C. In the third step, weight loss is found to be around 10% due to phase formation of the material at 580 °C because of decomposition of nitrates into oxides. A subsequent minor weight loss occurred after this range and then it became constant due to the phase formation. That means that the precursor generates a stable phase after the heat-treatment at higher than 600 °C. Also, from the TGA curve, it is seen that after 700 °C, there is a little increase in weight observed (∼1%) upto 1000 °C. This little increase might be due to the oxidation process involved at particular temperature[17]. Similar behaviour has been seen for $x = 0.05$.

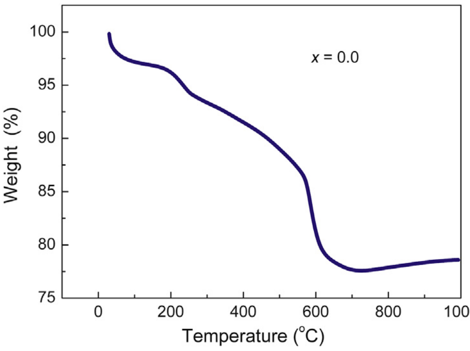

Fig. 1 Typical thermogram for $\mathrm{Li_{0.5}Ce_xFe_{2.5-x}O_4}$.

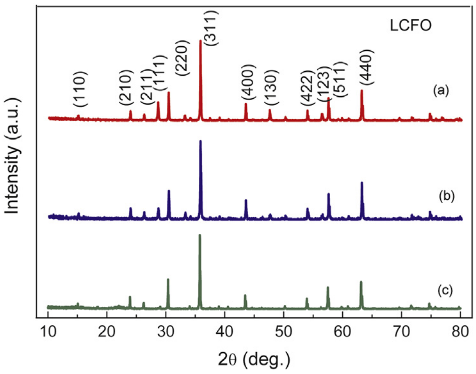

Fig. 2 XRD patterns of 900 °C $\mathrm{Li_{0.5}Ce_xFe_{2.5-x}O_4}$ system: (a) $x = 0.0$, (b) $x = 0.05$, (c) $x = 0.1$.

3.2. XRD studies

Fig. 2 illustrates the XRD patterns of the different compositions of the $\mathrm{Li_{0.5}Ce_xFe_{2.5-x}O_4}$ sintered at 900 °C. The samples show all the characteristic reflections of ferrite material with the most intense (311) peak, which confirms the formation of cubic inverse spinel structure. The results obtained by XRD are indexed using JCPDS reference code 01-088-0671. The phase pure crystallites are formed in a stable cubic structure of space group $p4332$ and lattice parameter was found with a refinement from celref3 software. We have calculated quantities such as lattice parameters, unit cell volume of all the materials and these are provided in Table 1. It can be observed explicitly from XRD patterns that Ce is completely substituted into lithium ferrite for cerium concentration Ce = 0.05. But in the case of Ce = 0.1, the

Table 1 Cell parameters and density of two samples $\mathrm{Li_{0.5}Ce_xFe_{2.5-x}O_4}$, where $x = 0$ and 0.05

Sample	Activation energy from impedance (eV)		Activation energy from modulus, E_P (eV) (±0.05)
	Dc conduction, E_σ (±0.05)	Cross over frequency, E_P (±0.05)	
LCFO-0.0	0.64	0.60	0.59
LCFO-0.05	0.69	0.65	0.65