Materials Chemistry and Physics 122 (2010) 133–137

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

Magnetic properties of nano-crystalline $Li_{0.35}Cd_{0.3}Fe_{2.35}O_4$ ferrite prepared by modified citrate precursor method

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ARTICLE INFO

Article history:
Received 26 June 2009
Received in revised form 22 January 2010
Accepted 23 February 2010

Keywords:
Nano-crystalline
X-ray diffraction
Transmission electron microscopy
Magnetization
Relaxation

ABSTRACT

Single phase nano-crystalline lithium cadmium ferrite $Li_{0.35}Cd_{0.3}Fe_{2.35}O_4$ is synthesized by a modified citrate gel precursor technique in different pH media. The modified citrate precursor technique reduces the formation of the impurity phase α-Fe_2O_3 in the inverse spinel phase of lithium ferrite. X-ray diffraction (XRD) and transmission electron microscopy (TEM) confirmed the average crystallite size. As-prepared sample shows the paramagnetic behaviour of M–H curve measured by vibrating sample magnetometer (VSM). The coercivity (H_c) and magnetization (M) both increase with decrease in temperature from 300 K to 80 K. Temperature dependent magnetic properties below the Curie point are defined by the Bloch's law and Neel relaxation relations. The effect of annealing on magnetic properties at different temperature is studied.

1. Introduction

Lithium ferrite belongs to a group of soft ferrite materials extensively used in many applications such as microwave devices, computer memory chips, magnetic recording media, radio frequency coil fabrication, transformer cores, rod antennas and many branches of telecommunication and electronic engineering [1–5]. This is due to its attractive features such as high Curie temperature, high saturation magnetization and square hysteresis loop. Nano-crystalline materials are showing great promise in industry and technology. This is mainly due to their unique properties that are not exhibited by bulk crystalline materials [6,7].

The structural and magnetic properties of spinel ferrites depend upon the method of preparation [8,9]. The conventional way to produce these materials is the solid state reaction method of oxides/carbonates followed by calcination at high temperature. The solid state reaction processing has some inherent disadvantages such as; chemical inhomogeneity, coarser particle size and introduction of impurities during the mixing/ball milling. The citrate gel precursor method is a well-established method for the synthesis of nano spinel type ferrites [10]. There are very few reports on the synthesis of single phase lithium cadmium ferrite by the citrate precursor technique. In this work we have studied the magnetic properties of nano $Li_{0.35}Cd_{0.3}Fe_{2.35}O_4$ prepared by a modified citrate gel precursor technique at two different pH media. X-ray diffraction confirms the pure phase formation of lithium cadmium ferrite sample prepared in a solution of pH 7. We have studied the effect of chemical control on pure phase formation and magnetic properties of lithium ferrites.

2. Experimental technique

Cadmium substituted lithium ferrite with composition $Li_{0.35}Cd_{0.3}Fe_{2.35}O_4$ was prepared by a citrate gel precursor technique at two different pH media say pH 1 and pH 7 sample. In this technique an oxidation–reduction reaction takes place in which the NO_3^- ion is the oxidant and the carboxyl group is the reductant. All high purity (more than 99% purity) chemicals $Fe(NO_3)_3{\cdot}9H_2O$, $Cd(NO_3)_2{\cdot}4H_2O$, $Li(NO_3)$ were used to synthesize the required compound. Previous studies have shown that a 1:1 mole ratio of metal and citric acid is the best ratio for the synthesis of nanosized ferrite particles [11]. The homogeneous aqueous solutions of each metal nitrate salt were formed in distilled water separately. Then we mixed all these solutions in citric solution drop by drop with constant stirring at room temperature. The homogeneous solution was obtained after mixing the aqueous solutions of the metal salts and citric acid with its natural pH equal to one. The solution was slowly evaporated for 24 h at 40 °C to form a viscous gel. Subsequently gel was placed in furnace at 100 °C to obtain porous powder followed by self combustion. In another case, the pH of the mixed solution was adjusted to 7 by adding ammonia solution and the final porous powder was obtained by following the same process. The powders of $Li_{0.35}Cd_{0.3}Fe_{2.35}O_4$ prepared at above mentioned pH were annealed at different temperatures viz. 500, 700, 800, 900 and 1000 °C.

2.1. X-ray diffraction studies

Phase analysis of ferrite samples prepared from different preparation methods route was investigated by X-ray diffraction (XRD Rigaku Miniflex II) with Cu Kα

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0254-0584/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.matchemphys.2010.02.057

radiation of wave length λ = 1.5406 Å. The scanning range was from 20° to 80° in step of 0.02°.

The average crystalline size was determined from the measured width of their diffraction curves using the Debye Scherrer's relation:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \tag{1}$$

where λ is the wavelength of the CuKα radiation (λ = 1.5406 Å) and β is the full width half maximum (FWHM) in radians calculated using Gaussian fitting. The contribution due to instrumental broadening has been taken into account in order to obtain the accurate crystallite size. In the present work instrumental broadening is corrected by using standard silicon sample.

The lattice constant was calculated using the relation:

$$2d \sin\theta = n\lambda$$

where $d = a/(h^2 + k^2 + l^2)^{1/2}$ for fcc system.

2.2. Magnetic measurements

Magnetic measurements were carried out using a vibrating sample magnetometer (Lake Shore 7305) for all samples over the temperature range from 300 K to 80 K. The magnetic properties such as saturation magnetization (M_s), coercivity (H_c) and retentivity (M_r) were calculated from M–H curves.

2.3. TEM measurement

The particle size of as-prepared samples was observed using a JEM-200CX transmission electron microscope.

2.4. FTIR measurement

FTIR spectra of all as-prepared samples were recorded in KBr medium in the wave number range 400–4000 cm^{-1} using a PerkinElmer FTIR (spectrum BX).

3. Results and discussion

3.1. Crystalline structure

In $Li_{0.35}Cd_{0.3}Fe_{2.35}O_4$ ferrite samples an inverse spinel phase is showing the main diffraction planes [2 2 0], [3 1 1], [4 0 0], [4 2 2], [5 1 1] and [4 4 0] with maximum diffraction intensity from [3 1 1] plane as shown in Fig. 1. A small amount of a α-Fe_2O_3 is also observed in pH 1 sample as depicted from plane [1 0 4] in XRD pattern. The average crystalline size of the as-prepared sample pH 1 is smaller in comparison to the pH 7 sample, which may be due to higher temperature during combustion. The larger crystallite size of the pH 7 sample may be due to generation of high temperature during the last stage of reaction. At pH 7 as-prepared sample shows the pure phase formation compared to pH 1 as-prepared sample as shown in Fig. 1. The crystallite sizes are about 10 nm and 30 nm for pH 1 and pH 7 sample respectively, measured by Debye Scherrer's relation and the value of lattice constant of pH 1 sample (8.365 Å) is higher than pH 7 sample (8.359 Å). The size of these nano particles is also confirmed by TEM images as shown in Fig. 2. The crystallite distributions were found to be in the range of 7–15 nm and 15–35 nm for pH 1 and pH 7 samples respectively. The crystallite size of samples, observed from XRD is in good agreement for both as-prepared samples. Most of the crystallite appear spherical in shape for pH 1 sample however some elongated crystallite are also present in the pH 7 sample. The bigger crystallite size in the pH 7 sample may be due to the presence of ammonia in solution, which increases the temperature during the exothermic self-propagating combustion. This increase in the temperature during the exothermic reaction for pH 7 sample can be defined on the basis of Kissinger's equation which suggests that the formation of the chelation complexes depends on the pH of the solution [12]. The addition of ammonia in reaction mixture decreases the activation energy, which is due to the higher enthalpy of the gel precursor that allow the easy rupture of the metal–oxygen bond in the gel precursor.

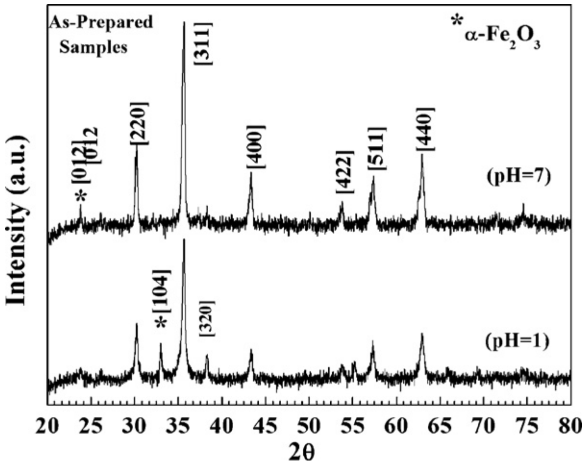

Fig. 1. X-ray diffraction patterns of as-prepared $Li_{0.35}Cd_{0.3}Fe_{2.35}O_4$ samples.

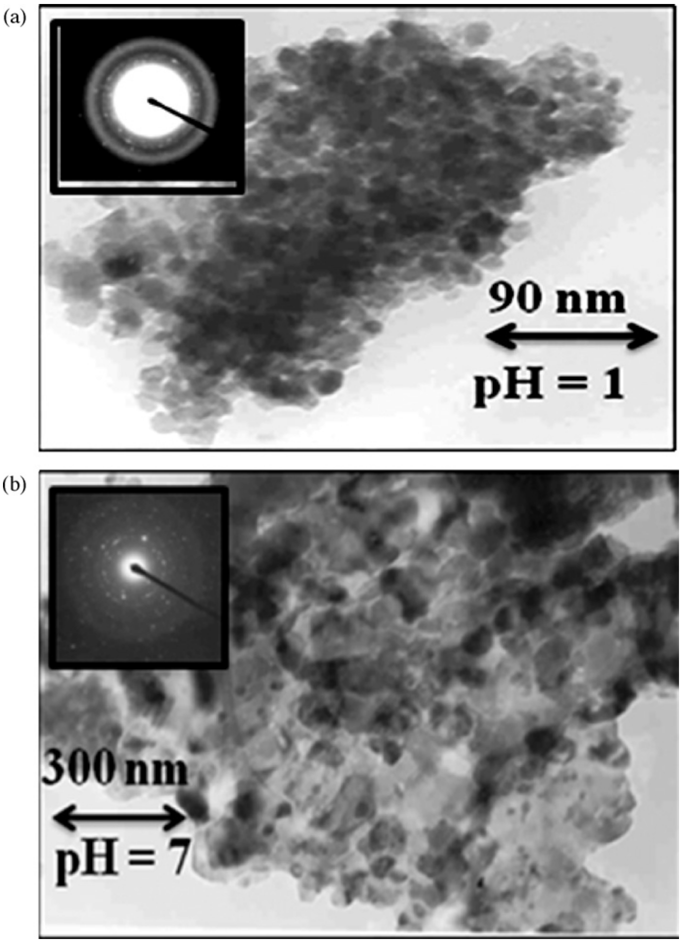

Fig. 2. Typical TEM image and diffraction pattern of as-prepared nano $Li_{0.35}Cd_{0.3}Fe_{2.35}O_4$ (a) pH 1, (b) pH 7 samples.

Fig. 3 shows the FTIR spectra of as-prepared samples in the range of (400–4000) cm^{-1}. As-prepared samples showed the characteristic band at about 3445, 1627 and 1394 cm^{-1} corresponding to vibrations of the O–H group, carboxyl group and NO_3^- ions, respectively. The presence of the characteristic bands of NO_3^- at 1384.6 cm^{-1} indicates that the NO_3^- exists as a group in the structure of citrate gel during the gelation of mixed solution formed from nitrates and citric acid. In FTIR spectra, there is one characteristic peak at 585 cm^{-1} which confirm the formation of ferrite in as-prepared samples.