Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 9931–9938

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Direct and facile synthesis of Li–Sr–Zn ferrites via low temperature solution combustion route

Jashanpreet Singh[a,*], B.S. Randhawa[a], Harpreet Kaur[a], H.S. Dosanjh[b]

[a]Department of Chemistry-UGC Sponsored Centre for Advanced Studies, Guru Nanak Dev University, Amritsar 143005, India
[b]Lovely Professional University, Phagwara 144411, India

Received 5 March 2015; received in revised form 13 April 2015; accepted 15 April 2015
Available online 23 April 2015

Abstract

Li–Sr–Zn nanoferrites i.e. $Li_{0.25}Sr_{0.5-x}Zn_xFe_{2.25}O_4$, where '$x$' varies from 0–0.5, have been synthesized using a low temperature solution combustion method which proves to be an efficient and economical technique for synthesizing these type of nanoferrites. The as-synthesized nanoferrites have cubic spinel structure as characterized by X-ray powder diffraction. Powder XRD and TEM (Transmission Electron Microscopy) characterization also evidence that the crystallite and particle size are in close agreement to each other. Mössbauer spectroscopy studies demonstrate that there is a gradual transition from ferrimagnetic to superparamagnetic character, which is also supported by the saturation magnetization and coercivity values. At room temperature, the nanoferrites were found to be superparamagnetic with negligible coercivities approaching towards zero while saturation magnetization values were found to be in the range 6.87–30.10 emu g^{-1}. The frequency dependent dielectric constant and loss values are in accordance with Koop's model. These nanoferrites show great potential in high density recordings, magnetic nanodevices and biomagnetic applications.

Keywords: A. Calcination; B. X-ray methods; C. Electrical properties; D. Ferrites

1. Introduction

Ferrites are mixed metal–iron (M–Fe) oxides having a variety of morphological features and are considered as important magnetic materials. They have been widely utilized as ferrimagnetic materials in different electronics industries [1]. The cubic spinel metal ferrites (MFe_2O_4, or $MO \cdot Fe_2O_3$) are important class of materials in which fcc (face centered cubic) close packing is formed by oxygen, and divalent metal ions (M^{2+}) and trivalent iron ions (Fe^{3+}) occupy interstitial tetrahedral or octahedral sites [2,3]. Adjustment of chemical identity of M^{2+} leads to variation of magnetic properties of MFe_2O_4, which can be efficiently utilized according to need. Due to this reason, nanoscale MFe_2O_4 materials are most frequently studied. Ferrite nanomagnets show potential technological applications as storage of information, electronic devices, drug delivery and medical diagnostics. Ferrite materials are also used in fabrication of magnetic cores for disk recordings and digital tapes [4,5], in levitated railway systems as repulsive suspension, magnetic refrigeration systems, ferrofluids and catalysis [6,7], in electromagnetic applications as ferrites can absorb electromagnetic radiation in microwave region [8]. Different techniques such as wet chemical methods [9–13], spray drying [14], and hydrothermal methods [15] have been employed, which lead to the formation of nanoscale ferrite particles. The conventional ceramic method which includes preparation of ferrites at high temperature results in loss of fine particle nature. Owing to the importance of nanocrystalline ferrites and technological importance of lithium ferrite, $Li_{0.5}Fe_{2.5}O_4$, a well-known ferrimagnetic compound in which trivalent Fe^{3+} ions are distributed both in tetrahedral (A) and octahedral (B sites) sites, $((Fe_{1.0})_A[Li_{0.5}\text{-}Fe_{1.5}]_BO_4)$, of spinel-related structure [16]. Here, the intersublattice interactions are antiferromagnetic while the intrasublattice interactions are ferromagnetic, and super-exchange interactions are reason for magnetic order. Other cations can be

---

*Corresponding author. Tel.: +91 9814757570.
E-mail address: jashan.chem84@yahoo.in (J. Singh).

http://dx.doi.org/10.1016/j.ceramint.2015.04.072
0272-8842/

substituted for Li ions and Fe ions to have spinel solids with a range of varying properties. In the present study, insertion of Sr and Zn with large ionic radii form spinel phases for which properties and cation distribution are the subject of interest. The adjustments made by these large ionic radii cations in this spinel structure are also an important factor. Earlier, single phase Ca doped Li–Zn nanoferrites were synthesized by a solution-combustion technique and characterized using different physico-chemical techniques, also describing their magnetic/dielectric behavior [17]. In continuation with this work, this manuscript describes the synthesis, microstructural, morphological and magnetic measurements on $Li_{0.25}Sr_{0.5-x}Zn_xFe_{2.25}O_4$ ($x=0$–0.5) nanoferrite system. In this way, we are presenting a systematic study on the magnetic properties of this ferrite system by means of magnetization and Mössbauer measurements.

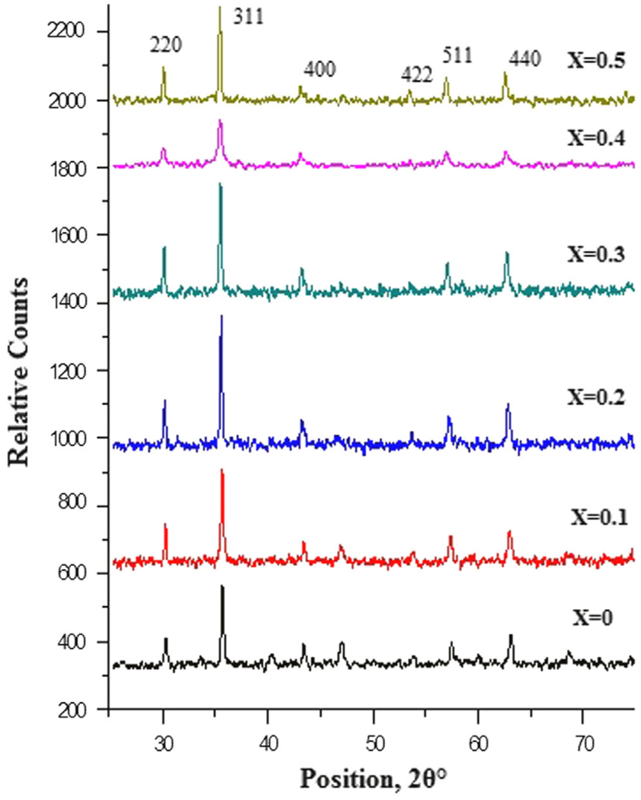

Fig. 1. X-ray powder diffraction patterns of $Li_{0.25}Sr_{0.5-x}Zn_xFe_{2.25}O_4$ with varying composition.

2. Material and methods

The ferrite powders ($Li_{0.25}Sr_{0.5-x}Zn_xFe_{2.25}O_4$, $x=0$, 0.1, 0.2, 0.3, 0.4, and 0.5) were prepared through the solution combustion method, which involves thorough mixing of stoichiometric quantities of aqueous solutions of lithium nitrate ($LiNO_3$), strontium nitrate [$Sr(NO_3)_2$], zinc nitrate [$Zn(NO_3)_2 \cdot 6H_2O$] and ferric nitrate [$Fe(NO_3)_3 \cdot 9H_2O$]. The reaction mixture was then concentrated on water bath and oxalyl dihydrazdie (fuel, synthesized from the reaction of one mole of diethyl oxalate and two moles of hydrazine hydrate) was added slowly until a solution-gel was obtained. The gel was taken in a nickel crucible and combusted at 600 °C for 3 h in a muffle furnace [18]. The brown powder thus obtained was grinded for approximately 5 h to get fine ferrite material. For the preparation of pellets, the powder was further pressed with an applied pressure of 5 MPa, where small amount of PVA was used as binder. The sintering of pellets was carried out at 950 °C for 5 h, since lithium is volatile above 1000 °C.

X-ray diffractometer (Rigaku Miniflex), operating with Cu-Kα radiation and equipped with a graphite crystal monochromator, (Step size=0.25°) was used to characterize the crystalline phases, broadening of diffraction lines and also to detect the average crystallite size. Crystallite size was calculated using Scherrer's formula i.e. $D=0.9\lambda/\beta 1/2\cos\theta$, where λ is X-ray wavelength, β is the line broadening at full width at half maximum (FWHM) in radians and θ isBragg's angle. Transmission Electron Microscopy (TEM) was employed to investigate the morphology of the mixed ferrite powders. The nanoparticles were dispersed on holey gold coated copper grids for TEM observation. Room temperature Mössbauer spectroscopic studies were recorded by using conventional constant acceleration spectrometer (MB-550) with ^{57}Co λ-ray source of 25 mCi embedded in rhodium matrix. Mössbauer spectra were analyzed by using Win-Normos fitting of various compositions. The isomer shift values are reported with respect to pure iron absorber. Magnetic measurements were carried out using room temperature Vibrating Sample Magnetometer (VSM) of Microsense Instruments. Dielectric studies were performed on Hioki 3530-20 LCR Hi-tester in the frequency range of 100 KHz to 5 MHz.

3. Results

The X-ray powder diffraction patterns recorded for various Li-ferrites with varying compositions ($Li_{0.25}Sr_{0.5-x}Zn_xFe_{2.25}O_4$)

Table 1
Structural parameters of the $Li_{0.25}Sr_{0.5-x}Zn_xFe_{2.25}O_4$ ferrite system.

Sample	Mol. weight	Lattice parameter (±0.001 A°)	d_{xrd} (±0.01 g cm^{-3})	d_{exp}	Porosity (%)	Crystallite size (XRD) (nm)	Particle size (TEM) (nm)
$X=0$	235.14	8.503	4.925	4.911	0.28	6	7
$X=0.1$	231.18	8.517	4.919	4.899	0.39	11	13
$X=0.2$	230.61	8.524	4.914	4.890	0.48	15	16
$X=0.3$	228.36	8.529	4.910	4.885	0.50	12	14
$X=0.4$	226.10	8.535	4.902	4.874	0.59	9	11
$X=0.5$	223.85	8.540	4.895	4.863	0.65	8	9