Journal of Alloys and Compounds 657 (2016) 95–108

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Incorporation of Cr^{3+} ions in tuning the magnetic and transport properties of nano zinc ferrite

B. Daruka Prasad [a, b, **], H. Nagabhushana [c, *], K. Thyagarajan [a], S.C. Sharma [d], C. Shivakumara [e], N.O. Gopal [f], B.M. Nagabhushana [g], Shyue-Chu Ke [h], R.P.S. Chakradhar [i], K.R. Prabhakara [j]

[a] Department of Physics, JNTUA College of Engineering, JNTUA-Ananthapur affiliated, Pulivendula 516 390, India
[b] Department of Physics, BMS Institute of Technology, VTU-Belagavi affiliated, Bengaluru 560 064, India
[c] CNR Rao Centre for Advanced Materials Research, Tumkur University, Tumkur 572 103, India
[d] Dayananda Sagar University, Shavige Malleshwara Hills, Kumaraswamy Layout, Bengaluru 560 078, India
[e] Solid State and Structural Chemistry Unit, Indian Institute of Science, Bengaluru 560 012, India
[f] Department of Physics, Vikrama Simhapuri University PG Centre, Kavali 524 201, India
[g] Department of Chemistry, MS Ramaiah Institute of Technology, Bengaluru 560 054, India
[h] Department of Physics, National Dong Hwa University, Hualien 97401, Taiwan, ROC
[i] CSIR-National Aerospace Laboratories, Bengaluru 560 017, India
[j] Department of Mechanical Engineering, R. V. College of Engineering, Bengaluru 560 059, India

ARTICLE INFO

Article history:
Received 13 April 2015
Received in revised form
5 September 2015
Accepted 30 September 2015
Available online 8 October 2015

Keywords:
Nano zinc ferrite
Magnetic materials
Dielectric properties
Ferrimagnetism

ABSTRACT

Cost effective and low temperature synthesis methods namely solution combustion and hydrothermal methods were used to prepare chromium incorporated nanocrystalline zinc ferrites. The effect of incorporation of low concentration Cr^{3+} ions on the structural, morphological, magnetic and transport properties of the zinc ferrite compounds were investigated. The crystalline nature and size variation with chromium content were valid from powder x-ray diffraction. Particles size and crystallite size variation were valid from scanning electron microscopy and transmission electron microscopy respectively. With the increase in chromium incorporation, the crystallite and particles sizes were decreased. Fourier transform infrared spectroscopy (FTIR) studies confirmed the presence of strong metal-oxygen bonds. The elastic properties of the materials in both the methods were estimated by FTIR studies. Magnetic properties namely saturation magentization, remanent magnetization and coercivity values were decreased with increase in Cr^{3+} ions concentration. The dielectric properties of the samples decreased with increase in the Cr^{3+} ions. The dielectric constant was observed to be of the order of 10^6 at low frequency and almost 1 at higher frequency range. The activation energy estimated using Arrhenius plots was of the order of 0.182 eV and 0.368 eV respectively for the compounds prepared by solution combustion and hydrothermal methods. The emission spectra of the samples excited at 344 nm were reported using photoluminescence (PL) spectroscopy. Further, the approximate energy band gap(E_g) was estimated from PL studies. The E_g of the materials were lie in the range of 2.11−1.98 eV.

1. Introduction

Ability of materials to change their properties at nanoscale has opened up the possibility of making devices, instruments, consumer goods etc. to function in much better than was with its bulk counterpart. Nanocrystalline ferrites have been attracted because of their promising technological applications. Nano zinc ferrites and their composites have received much attention as a promising materials for advanced applications viz strain sensing, actuating, data storage applications and microwave control components like isolators and phase shifters [1–3]. In recent years, zinc ferrite (ZF) nanoparticles have been extensively studied due to their low coercitivity, high magnetocrystalline anisotropy and moderate

* Corresponding author. CNR Rao Centre for Advanced Materials Research, Tumkur University, Tumkur 572 103, India.
** Corresponding author. Department of Physics, BMS Institute of Technology, VTU-Belagavi affiliated, Bengaluru 560 064, India.
E-mail addresses: darukap@bmsit.in (B.D. Prasad), bhushanvlc@gmail.com (H. Nagabhushana).

http://dx.doi.org/10.1016/j.jallcom.2015.09.270
0925-8388/

saturation magnetization. The zinc ferrite belongs to the spinel structure with general formula of AB_2O_4 which crystallizes in many possible intermediate distributions represented by $(A_{1-\lambda}B_\lambda)(A_\lambda B_{2-\lambda})O_4$ where λ is called inversion parameter [4]. In order to tailor the magnetic, dielectric and magnetoelastic properties of nano zinc ferrite, incorporation of chromium into Fe sites has been proposed. These materials are of particular interest because Cr^{3+} ions have very strong preference for the octahedral sites [5,6]. A few previous investigations of chromium zinc ferrites have been reported, but they mainly concentrated on the Cr-rich composition [7–9]. Various preparation methods have been developed to produce ZF nanoparticles, such as micro-emulsion [10], sol–gel [11,12], hydrothermal [13–15], coprecipitation [16], thermal plasma syntheses [17,18] etc. The choice of efficient homogeneous phase and economically viable synthesis of ZF nanocrystals is of great interest. Spinel structured compounds will have octahedral (A-site) and tetrahedral (B-site) sites. In which Zn^{2+} prefers the tetrahedral sites and Fe^{3+} ions prefer the octahedral sites. In nanoscale, due to cation distribution, Fe ions exist both in octahedral and tetrahedral sites. The percentage of Fe ions in octahedral (Fe^{3+}) and tetrahedral (Fe^{2+}) sites varies and it depends on the method of preparation, heat treatment to the samples and stoichiometry considered during the preparation. Hence a Fe^{2+} and Fe^{3+} ions exists in the compound. Further, in many manuscripts the authors explained the hopping conduction between these ions. The dopants at octahedral site affects the hopping conduction between $Fe^{2+} \leftrightarrow Fe^{3+}$. The dopants to octahedral sites decrease the hopping between these ions [19]. In nanoelectronics applications like CMOS- compatible, scalable deposition and to improve the inductance density of thin films of zinc ferrites with high permeability, low eddy current losses and low conductivity is must [20]. Because of partial inversion in the spinel structure, zinc ferrite is suitable for such type of nanoelectronic applications. Cr^{3+} is chosen as dopant to tune its conductivity behaviour such that same composition when prepared in thin films it may be useful for nanoelectronic devices. In this work, the comparative study on the structure, morphology, magnetic and transport properties of $ZnFe_{2-x}Cr_xO_4$ (x = 0, 0.01, 0.03, 0.05 and 0.07) nanoparticles; synthesized by solution combustion (SCS) and hydrothermal (HYDS) methods has been reported. The SCS route is employed because of its self-sustainable reaction, obtaining the high purity and chemically stable homogeneous final product without further calcination. And HYDS method is very versatile at low temperature synthesis, shape can be tuned, owing to its economy, ecofriendly and the high degree of compositional control.

2. Experimental

Nanoparticles of chromium incorporated zinc ferrites (ZF) were prepared by the SCS and HYDS methods. In SCS technique, the stoichiometric quantities of analytical grade zinc nitrate (Merck), ferric nitrate (Merck), freshly prepared chromium nitrate obtained from chromium (III) oxide (Sigma–Aldrich) and concentrated HNO_3 as precursors and oxalyldihydrazide as fuel were diluted with distilled water and subjected to low temperature combustion. In

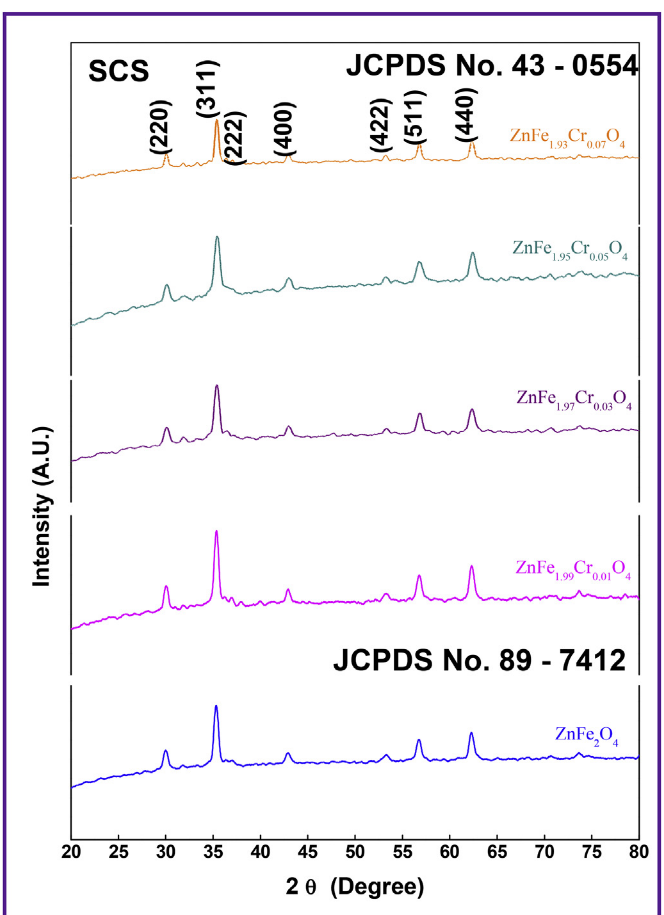

Fig. 1. PXRD of $ZnFe_{2-x}Cr_xO_4$ (x = 0.01–0.07) prepared by SCS method.

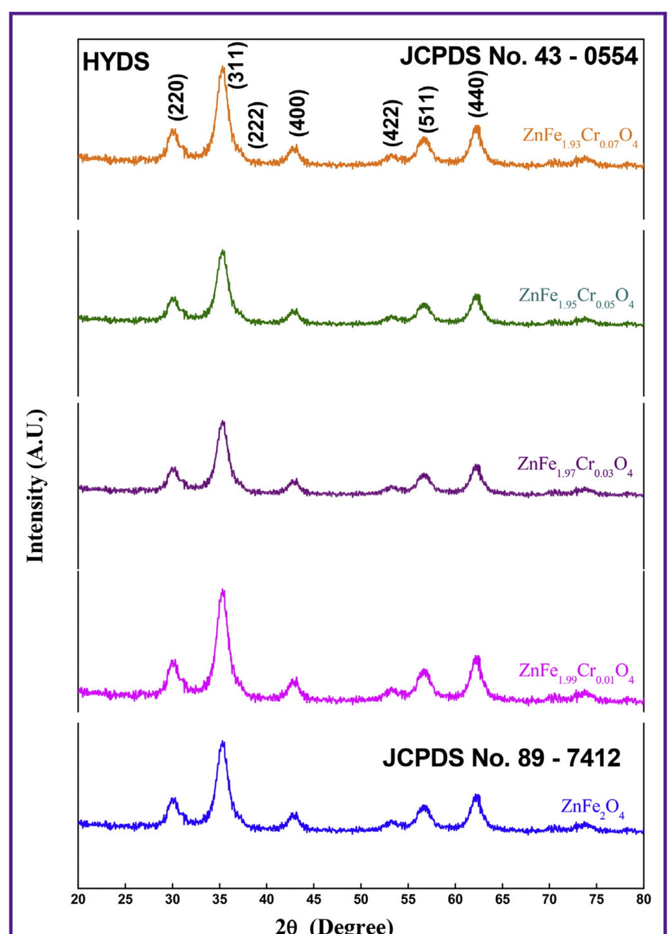

Fig. 2. PXRD of $ZnFe_{2-x}Cr_xO_4$ (x = 0.01–0.07) prepared by HYDS method.