Journal of Magnetism and Magnetic Materials 379 (2015) 179–185

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

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

Study of conduction phenomena in indium substituted Mn–Zn nano-ferrites

Surender Kumar [a,*], Tukaram J. Shinde [b], Pramod N. Vasambekar [c]

[a] Department of Physics, Pandit Anant Ram Sanatan Dharam College, Baroh 176054, India
[b] Department of Physics, KRP Kanya Mahavidyalaya, Islampur 415409, India
[c] Department of Electronics, Shivaji University, Kolhapur 416004, India

ARTICLE INFO

Article history:
Received 13 September 2014
Received in revised form
10 November 2014
Accepted 15 December 2014
Available online 16 December 2014

Keywords:
Ferrites
Coprecipitation
Dc resistivity
Thermoelectric power

ABSTRACT

Nanocrystalline Indium substituted Mn–Zn ferrites were prepared by oxalate coprecipitation technique in combination with microwave heating. X-ray diffraction and scanning electron microscopy was used to study nano-structural parameters such as crystallite size, lattice constant, X-ray density, observed density and morphology of the synthesized nanopowders. The lattice constant, crystallite size and X-ray density increased with increase in Indium concentration. Thermal variation of dc resistivity was studied by two probe method. The resistivity decreased exponentially with increasing Indium concentration and the change of slope of dc resistivity plot was observed at Curie temperature. Small polaron hopping between Fe^{2+} and Fe^{3+} ions at octahedral sites was established. Substitution of Indium ions increased the dc resistivity. Differential method was used to study thermoelectric power. Thermo-emf remained constant with increasing temperature; the n-type conduction mechanism and localization of charge carriers at lattice sites due to strong electron–phonon interaction was established.

1. Introduction

The rapid technological development aiming at miniaturization, lighter weight, integration, and multifunction devices have fueled the demand for Mn–Zn ferrites, which are applied as core materials for transformers in switching mode power supplies, pulse transformers, memory-core devices and dc/dc converters. These applications are based on low core loss, high initial magnetic permeability, large saturation magnetic flux density, and high resistivity of Mn–Zn ferrites [1–3]. Polycrystalline ferrites are excellent dielectrics with high resistivity; they offer wide range of technological applications from microwave to radio wave frequencies [2].

The presence of metal ions with multiple valence states on identical crystallographic sites is responsible for electrical properties. Primarily, the electrical conduction in spinel ferrites is attributed to electron/small polaron hopping mechanism between Fe^{3+} and Fe^{2+} ions present on equivalent lattice sites. However in mixed ferrites, presence of multivalent metal ions such as Mn (Mn^{2+}, Mn^{3+}), Ni (Ni^{2+}, Ni^{3+}), Yb (Yb^{2+}, Yb^{3+}) and Co (Co^{2+}, Co^{3+}) can also influence electrical properties. The resistivity of spinel ferrites range widely from $\sim 10^4$ to 10^9 Ω cm at room temperature [3]. Availability of ions in more than one valence state depends on the concentration of cations and preparation conditions. The face centered cubic spinel structure of ferrites has two types of interstitial sites; octahedral and tetrahedral sites. The hopping between tetrahedral–tetrahedral sites does not exist because iron at tetrahedral site exists only in Fe^{3+} state so octahedral–octahedral hopping is the only possibility [4]. The ratio Fe^{2+}/Fe^{3+} in the octahedral site determines the probability of hopping between Fe^{2+} and Fe^{3+}. In addition to the composition of spinel ferrites other microstructural parameters also influence the electrical properties. In fact, the dc resistivity of ferrites is a complex interplay of factors such as composition, density, porosity, grain size, cation distribution, crystal structure perfection and microstructural homogeneity and impurity levels. Specifically, the dc resistivity of ferrites is inversely proportional to grain size and density. These materials have conductive grains surrounded by resistive grain boundaries among which pores of various sizes and shapes are distributed. The porosity increases the DC resistivity of ferrites since the pores offers additional resistance to flow of charge through the material [5–7]. The resistivity of grains is much smaller than that of grain boundaries. Therefore, the dominant contribution to the resistivity comes from high-resistive grain boundaries [8]. Small grains have larger volume of insulating grain boundaries and hence greater energy barriers for electron/small polaron conduction leading to higher resistivity. The grain boundaries are the region of mismatch between the energy states

* Corresponding author.
E-mail address: surender.postbox@gmail.com (S. Kumar).

http://dx.doi.org/10.1016/j.jmmm.2014.12.031
0304-8853/

of adjacent grains and hence acts barrier to the flow of electrons/small polarons. Additionally, small grain size helps in reducing Fe^{2+} ions by allowing fast movement of oxygen thereby keeping iron in Fe^{3+} state [9]. The concentration of charge carriers does not change with temperature variation and the Increase/decrease in resistivity of spinel ferrites is attributed to increase/decrease in drift mobility of the charge carriers. Another important aspect of the conduction mechanism in ferrites is the activation energy; higher activation energy refers to higher resistivity. The effect of the Fe^{2+} can be gauged from the fact that the presence of 0.3% Fe^{2+} in ferrites can reduce dc resistivity by a factor of more than two order of magnitude [5]. In ferrites containing Zinc, Zinc loss commences on treating the ferrite powders above 950 °C; this generates Fe^{2+} ions which increases the hopping between Fe^{2+} and Fe^{3+} ions ensuring reduction in the resistivity [10,6].

The temperature variation of dc resistivity provides useful information about the charge carriers and the effect of various cationic substitutions. Laxman et al. [11] prepared In^{3+} substituted Mg–Mn ferrites by conventional ceramic technique; dc resistivity was found to increase increasing In^{3+} concentration. At lower concentrations In^{3+} occupy tetrahedral sites and push Mn^{2+} ions into octahedral sites. This decreases the number of Fe^{3+} ions at octahedral sites and reduces hopping probability between Fe^{3+} and Fe^{2+} ions thereby leading to rise in resistivity. Nam et al. [12] prepared Ni–Cu–Zn ferrites using solid state reaction method and reported peak in dc resistivity with increasing Cu concentration; the activation energy was in the range 0.382 to 0.705 eV. Nongjai et al. [13] observed increase in dc resistivity with increasing In^{3+} concentration in Co–In ferrites prepared by citrate-gel method; this was attributed to smaller grains which reduce the grain to grain surface contact area and the motion of charge carriers. The high resistivity and low dielectric loss ferrites are suitable for power application at higher frequencies. Islam et al. [14] observed exponential increase in resistivity with increasing Gd concentration in Mn–Zn–Gd ferrites; they reported that value of activation energy in the ferromagnetic region is lower than that of the paramagnetic region. Shirsath et al. [15] studied Al^{3+} substituted Mn–Zn ferrites by sol–gel auto combustion technique; the reported activation energy was in the range 0.462–.497 eV and resistivity increased with increasing Al^{3+} concentration. The activation energy is associated with the variation of mobility of the charge carriers rather than with their concentration.

Hall effect and thermoelectric power are used to study the conduction mechanism in semiconductors but the spinel ferrites are low mobility materials and it is difficult to study the hall effect. Hence thermoelectric power is the only alternative. Thermoelectric power enables determination of type of charge carriers: n-type or p-type, and the carrier concentration. Thermoelectric power studies are effectively employed to understand the dynamics of electrical conduction in ferrites. Ravinder et al. [16] attributed the negative sign of Seebeck coefficient of Mg–Li ferrites to n-type conduction. The value of Seebeck coefficient was in the range -231 to $-982\ \mu$V/K and charge carrier mobility was in the range $\sim 10^{-4}$ to 10^{-11} cm^2/Vs. Substitution of Zn in Mg–Li ferrites by In^{3+} another work by Ravinder et al. [17] n-type conduction mechanism was observed for Li–Ge ferrites; Thermoelectric power increased initially, peaked and then decreased with further increase in temperature. Ladgaonkar et al. [18] studied Nd^{3+} substituted Zn–Mg ferrites; The negative Seebeck coefficient was attributed to n-type charge carriers participating in hopping process. The charge careers were localized at lattice sites due to strong electron–phonon interaction. Ata et al. [19] prepared Li–Co ferrites by double sintering method and the negative sign of thermoelectric power confirmed n-type conduction and α was temperature independent.

Microwave synthesis has emerged as an attractive technique for materials synthesis [20]. Recent activism in microwave synthesis of materials aimed at achieving improved electrical, optical, thermal and mechanical properties. The prominent difference between conventional heating and microwave heating is the heating mechanism. Heat generated in conventional electrical furnace diffuses into the sample via radiation, conduction and convection; this leads to internal stresses and temperature gradients in the sample. As compared to this, heat production in microwave irradiated samples remains confined to the sample [21]. The microwave heating occurs via dielectric losses, in which the heat is produced by rapid rotation of dipoles at microwave frequencies. The rotation of dipoles within the material encounters resistance and heats up the material due to frictional heating. Thus microwave heating is volumetric and internal heating process that allows uniform heating. Microwave susceptor is used when synthesis method depends on microwave transparent precursors; SiC plates and rods, Y_2O_3 stabilized ZrO_2 refractory tiles and powdered graphite has been reported as efficient microwave susceptors [22, 21]. Transition metal oxides are good microwave absorbers whereas oxides of non-transition metals are poor microwave absorbers [23]. This work aims at systematic study of electrical properties and the underlying conduction mechanism of the In^{3+} substituted nanocrystalline ferrites prepared by wet chemical synthesis followed by microwave heating.

2. Experimental

Nanocrystaline $Mn_{0.4}Zn_{0.6}In_yFe_{2-y}O_4$ ($y=0$, 0.035, 0.070, 0.100) were prepared by oxalate co-precipitation technique followed by microwave heating. The synthesis method has been discussed elsewhere [20], however in brief, Manganese sulfate monohydrate ($MnSO_4.H_2O > 99\%$, Merck), Iron (II) sulfate heptahydrate ($FeSO_4 \cdot 7H_2O >$ 99%, Merck), Zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O >$ 99%, Merck), anhydrous Indium Sufate ($In_2(SO_4)_3 >$ 99%, Hi-Media) and Di-ammonium oxalate monohydrate ($(NH_4)_2C_2O_4 \cdot H_2O$) were used as starting materials. The aqueous solution of Di-Ammonium oxalate was rapidly added to the solution of metal sulfates under continuous stirring at 45 °C. Stirring was continued for 30 min for complete formation of precipitates. Precipitates were washed several times and then dried in an oven at 100 °C for 8 h. In-house built microwave heating setup was used to produce ferrite powders from dried yellow precipitates. Metal oxalates are poor microwave absorbers; therefore Aluminum metal powder was used as microwave susceptor. This setup was now placed on the turn table of commercial microwave oven (Onida, 25XL Power Convection) operated at frequency of 2.45 GHz with maximum output power of 900 W. The oven was operated at 60% of optimum power for 630 s to raise the temperature of the precursors to 450 °C.The brick was immediately brought out of the oven and allowed to cool.

The XRD patterns of nano-ferrites were recorded in the scattering range (2θ) of 10° −80°, scan rate of 0.05° per second and a primary beam power of 40 kV, 30 mA using a Bruker AXS D8 Advance X-ray diffractometer with Cu-Kα radiation ($\lambda=1.54058$ Å). The microstructure and morphology of nanocrystalline ferrites were investigated by scanning electron microphotographs under JEOL JSM-6610LV scanning electron microscope. Polyvinyl alcohol was added as binder to the ferrite powder in an agate mortar and thoroughly mixed. The powder was pressed in a pellet die under a force of 6 t for 3 min under a hydraulic press. The pellets (thickness 2 mm and diameter 10 mm) were sintered at 400 °C for 2 h.

2.1. Results and analysis

Fig. 1 shows X-ray diffraction patterns of In^{3+} substituted Mn–Zn ferrites. The peaks were indexed as pure spinel phase of space