Frequency dependent dielectric measurements of Cd$^{2+}$ doped Mn-Zn nano ferrites prepared by sol gel and coprecipitation methods

A Humaira$^1$ and M Asghari$^{1*}$

$^1$Thermal Transport Laboratory, Department of Materials Engineering, School of Chemical and Materials Engineering (SCME), National University of Sciences and Technology, H-12, Islamabad.

$^{*}$E-mail: tpl.qau@usa.net

Abstract

Ferrite powders of Mn-Zn doped with Cd$^{2+}$ (Mn$_{0.5}$Cd$_{x}$Zn$_{0.5-x}$Fe$_2$O$_4$) were prepared by the sol gel auto-combustion and coprecipitation methods. The effect of Cd$^{2+}$ doping on the crystalline phase formation was investigated by X-ray diffraction which confirms the spinel structure of prepared samples. Crystallite size found to be lower for samples prepared by coprecipitation method. The samples prepared using coprecipitation, found to be denser as compared to sol gel method. SEM analysis confirmed the nano structure of the prepared samples. Dielectric properties were studied using impedance analyzer (20 Hz – 5 MHz) and RF material analyzer (1 MHz - 3 GHz) respectively. DC electrical measurements showed highly resistive nature of the prepared samples and values are high for samples prepared from sol gel method. Impedance spectroscopic analysis was carried out in the frequency range from 20 Hz to 5 MHz for the prepared samples, showing resistance of grain boundary is higher than grains. Impedance plane plots gave information about the resistive and reactive parts of impedance. The presence of semicircular arcs at lower frequency side, confirms that the high resistance of samples is due to increase in the number of grain boundaries in the nano synthesised samples.

Key words: Nano structure; Sol gel combustion; Coprecipitation; X-ray diffraction; Dielectric constant

1. Introduction

Nano scale polycrystalline ferrites with unique electrical and magnetic properties are of great interest for scientist and engineers [1-3]. Even after more than half of the century the scientist, researchers, technologist, and engineers are still excited in various types of nanocrystalline as well as bulk ferrite materials. Transition metal oxides (MFe$_2$O$_4$) are magnetic materials with cubic spinel structure and have been used in various electronic and electrical applications for the last decade. The high permeability in the radio frequency region, make them suitable for use in electronic devices [4]. The Mn-Zn ferrites are soft ferrite having low magnetic coercivity and high electrical resistivity. The high electrical resistivity and good magnetic properties make it excellent core material for use in electronic and telecommunication applications [5]. The dielectric behavior of polycrystalline soft ferrites is very important to understand the polarization mechanism. The electrical conductivity and dielectric properties greatly depends on the method of preparation, sintering conditions and doping of cations [6]. The change in method of preparation and chemical composition alters the physical properties for use in a particular application. The nano phases obtained using soft chemical methods such as sol gel auto-combustion or coprecipitation methods have an edge over conventional ceramic route with improved properties [6]. Ferrites are very effective as microwave absorbers due to their low cost, low eddy loses and high resistivity. The addition of non magnetic ions (i.e. Zn$^{2+}$, Cd$^{2+}$) in small amount results in the modification of saturation magnetization [5]. Batoo et al. [7] have investigated the influence of Al doping on the structural and electrical properties of Ni–Cd mixed ferrite. Bhu et al. [8] have studied structural and magnetic properties of Gd$^{3+}$ doped Ni-Cd mixed ferrites. Nikumbh et al. [9] have studied the structural, electrical and magnetic properties and cation distribution of cadmium-substituted nickel ferrite. Very few studies...
are reported on the doping of \text{Cd}^{2+} ions in manganese and zinc ferrites [10]. In the present work comparison of \text{Cd}^{2+} doping on the Mn-Zn mixed ferrites has been presented over the wide range of frequency. The change in various physical parameters and their characteristic properties that affect the performance of these materials can be known and explained using complex impedance spectroscopy. In the present paper we have studied the effect of preparation technique on the structural, electrical and impedance properties of Mn\textsubscript{0.5}Zn\textsubscript{0.5}Cd\textsubscript{2}Fe\textsubscript{2}O\textsubscript{4} (x = 0, 0.15, 0.25, 0.35) soft ferrites as a function of composition and frequency at room temperature.

2. Experimental details

2.1. Sample preparation

A series of nano crystalline samples with general formula Mn\textsubscript{x}Zn\textsubscript{0.5-x}Cd\textsubscript{2}Fe\textsubscript{2}O\textsubscript{4} (x = 0, 0.15, 0.25, 0.35) were synthesized using sol gel auto-combustion and coprecipitation methods [5, 8]. The starting materials, for sol-gel auto combustion method, were of analytical grade Mn(NO\textsubscript{3})\textsubscript{2},4H\textsubscript{2}O, Zn(NO\textsubscript{3})\textsubscript{2},H\textsubscript{2}O, Cd(NO\textsubscript{3})\textsubscript{2},4H\textsubscript{2}O, Fe\textsubscript{2}(NO\textsubscript{3})\textsubscript{3},9H\textsubscript{2}O and C\textsubscript{6}H\textsubscript{5}O\textsubscript{2}H\textsubscript{2}O (99.9%). Metal nitrates and citric acid were dissolved in deionized water in 1: 1.5 molar ratios at room temperature. The pH of solution was adjusted to 7 using ammonia solution. The solution was allowed to evaporate and transform into gel on heating at 363 K. Further heating allows the gel to burn in a self ignition manner and form the fluffy loose powder on complete combustion followed by heating at 473 K for 4 h to remove organic materials. The as-burnt precursor powder was ground well in a pestle mortar and then sintered at 1073 K for 8 h. The sintered powders were then pelletized in circular disks of 10 mm diameter by applying a uniaxial load of 5 kN.

\text{Nano-crystalline Mn}_{0.5}\text{Zn}_{0.5}\text{Cd}_{2}\text{Fe}_{2}\text{O}_{4} (x = 0, 0.15, 0.25, 0.35) particles were synthesized by chemical co-precipitation method [11, 12] using AR grade Mn(NO\textsubscript{3})\textsubscript{2},4H\textsubscript{2}O, Zn(NO\textsubscript{3})\textsubscript{2},H\textsubscript{2}O, Cd(NO\textsubscript{3})\textsubscript{2},4H\textsubscript{2}O and Fe\textsubscript{2}(NO\textsubscript{3})\textsubscript{3},9H\textsubscript{2}O. For synthesis x = 0 composition, 0.05molar solutions of Mn(NO\textsubscript{3})\textsubscript{2},4H\textsubscript{2}O, 0.05 molar Zn(NO\textsubscript{3})\textsubscript{2},H\textsubscript{2}O and 0.2 molar Fe(NO\textsubscript{3})\textsubscript{2},9H\textsubscript{2}O were mixed in their stoichiometric ratio and homogenized at 358 K. The 2 M solution of NaOH was added to adjust the pH of the solution between 10.5 -11.5. The mixture was then heated at 363 K for about 1h. The precipitates were thoroughly washed with distilled water until the washings were free from sodium and chloride ions. The product was dried in an electric oven at 378 K for overnight to remove water contents. Ferrite powders were heated at 1073 K for 8 h. These were then pelletized in circular disks of 10mm diameter by applying a uniaxial load of 5kN using hydraulic press. The samples prepared from both techniques were then characterized through various techniques.

2.2 Characterizations

The crystalline phases of the prepared samples were determined using the X-ray diffraction (XRD) technique. XRD patterns were taken using Cu Ka (\(\lambda = 1.5406 \text{ Å}\)) radiation at room temperature. Scanning was performed from 20° to 80° at a step size of 0.02°s\textsuperscript{-1}. The crystallite size (t\textsubscript{hkl}), lattice parameter (a), X-ray density (\(\rho_{a}\)) and porosity (P) were calculated using simple formulae [13]. The surface morphology was performed using a scanning electron microscopy (JEOL-instrument JSM-6490A). The DC electrical resistivity was obtained by a simple two-probe method within temperature range 300 – 573 K. The relationship between electrical resistivity (\(\rho\)) and temperature [13] may be expressed as

\[
\rho = \rho_{\text{exp}} \left(\Delta E/k_{B}T\right)
\]

where \(\Delta E\) is the activation energy in (eV) for conduction, \(k_{B}\) is the Boltzmann constant and \(T\) is the temperature in Kelvin (K).

Dielectric and impedance spectroscopic measurements were carried out using WAYNE KERR LCR METER (6440B) in the frequency range from 20 Hz to 5 MHz at room temperature. The samples were pressed into circular disc shaped pellets, and placed in a specially designed sample holder. The real part of the dielectric constant (\(\varepsilon'\)) was calculated by the relation [13, 7]

\[
\varepsilon' = C_{d}/\varepsilon_{0}A
\]
where \( C_p \) is the parallel plate capacitance in Farad, \( d \) the thickness of the pellets in m, \( A \) the cross-sectional area of a flat surface of the pellet sample in \( m^2 \) and \( \varepsilon_0 \) is the permittivity of free space, equal to \( 8.854 \times 10^{-12} \) F/m. The dielectric loss tangent (tan \( \delta \)) which is the loss of energy from the applied field into the sample in the form of heat, can be determined in terms of real and imaginary parts of dielectric constant as

\[
\tan \delta = \frac{D}{\varepsilon'} = \frac{\varepsilon''}{\varepsilon'}
\]  

Impedance measurements were performed in the frequency range from 20 Hz to 5 MHz at room temperature by taking the absolute value of impedance \( |Z| \) with varying complex angle \( \theta \). The real and imaginary parts of impedance can be written as:

\[
Z' = |Z| \cos \theta
\]

\[
Z'' = |Z| \sin \theta
\]

The variation in dielectric properties in the frequency range of 1 MHz to 1 GHz were also studied using RF material analyzer.

3. Results and discussion
3.1 Structural properties

The X-ray diffraction pattern of nano ferrite samples with composition \( \text{Mn}_{0.5}\text{Zn}_{0.5-x}\text{Cd}_x\text{Fe}_2\text{O}_4 \) (\( x = 0, 0.15, 0.25, 0.35 \)) are shown in Figure 1.

![X-ray diffraction patterns](image)

Figure. 1 Indexed X-ray diffraction pattern for the \( \text{Mn}_{0.5}\text{Zn}_{0.5-x}\text{Cd}_x\text{Fe}_2\text{O}_4 \) nano ferrites.

The XRD data were analyzed by X’ Pert High Score software which shows that all the samples exhibit single-phase and polycrystalline FCC spinel structure. Absence of any extra peak implies that \( \text{Cd}^{2+} \) ions have been dissolved in to complete spinel structure. The lattice constants were determined using data obtained from XRD patterns. The slight increase in lattice constant is observed with increase in \( \text{Cd}^{2+} \) concentration which is due to the replacement of \( \text{Zn}^{2+} \) ion (0.83 Å) of small ionic radius with \( \text{Cd}^{2+} \) (0.97 Å) ion of slightly large ionic radius. The results are in good agreement with the reports in the literature [6]. The values of X-ray density (theoretical density) and apparent density (experimental density) of the samples are listed in Table 1.
Table 1 The average crystallite size ($t_{(ave)}$), lattice constant ($a$), X-ray density ($D_x$), physical density ($D_m$), DC electrical resistivity ($\rho_{dc}$), and activation energy ($\Delta E$) of the $\text{Mn}_{0.5}\text{Zn}_{0.5-x}\text{Cd}_x\text{Fe}_2\text{O}_4$ nano ferrites with varying Cd$^{2+}$ ions concentrations $0 \leq x \leq 0.35$ prepared by sol gel and coprecipitation methods respectively.

| Composition | $x = 0$ | $x = 0.15$ | $x = 0.25$ | $x = 0.35$ |
|-------------|---------|------------|------------|------------|
| $t$ (average) nm | 24 | 31 | 40 | 50 |
| $a$(Å) | 8.479 | 8.488 | 8.497 | 8.488 |
| $D_x$(g-cm$^{-3}$) | 5.15 | 5.28 | 5.37 | 5.49 |
| $D_m$(g-cm$^{-3}$) | 3.31 | 3.35 | 3.35 | 3.30 |
| $P$ (fraction) | 0.36 | 0.37 | 0.38 | 0.40 |
| $\rho$(Ω-cm)at 373 K | $5.1 \times 10^8$ | $5.8 \times 10^{10}$ | $2.2 \times 10^{11}$ | $3.3 \times 10^{10}$ |
| $\Delta E$ (eV) | 0.36 | 0.37 | 0.38 | 0.40 |

| Coprecipitation | $x = 0$ | $x = 0.15$ | $x = 0.25$ | $x = 0.35$ |
|-----------------|---------|------------|------------|------------|
| $t$ (average) nm | 14 | 17 | 19 | 22 |
| $a$(Å) | 8.415 | 8.421 | 8.438 | 8.437 |
| $D_x$(g-cm$^{-3}$) | 5.26 | 5.41 | 5.48 | 5.59 |
| $D_m$(g-cm$^{-3}$) | 3.28 | 3.44 | 3.60 | 3.50 |
| $P$ (fraction) | 0.37 | 0.36 | 0.34 | 0.37 |
| $\rho$(Ω-cm)at 373 K | $7.13 \times 10^8$ | $5.87 \times 10^9$ | $1.44 \times 10^{10}$ | $3.08 \times 10^9$ |
| $\Delta E$ (eV) | 0.71 | 0.55 | 0.58 | 0.70 |

X-ray density increased with addition of Cd$^{2+}$ ions concentration. This may be due to the fact that atomic weight and density of Cd atoms are 112.4 amu and 8.65gm/cm$^3$ respectively, which are greater than those of Zn atoms (65.4 amu and 7.14 gm/cm$^3$). The apparent density is less than X-ray density due to presence of pores which depends on the sintering conditions [14]. The porosity increases because X-ray density increased and measured density decreased with the addition of Cd$^{2+}$ ions.

The morphology of the samples prepared by both techniques was examined by scanning electron microscopy (SEM). The microstructural analysis gives information about the type and size of grain growth in the samples, which influence the physical and electrical properties of materials. The SEM images are shown in Fig. 2. The nano size nature of the prepared samples is clear from the micrographs and agglomeration of particles gives the magnetic nature of prepared samples. The comparison of micrographs for $x = 0.25$ prepared by both methods indicates that samples prepared by coprecipitation are more uniform, homogenous and smaller in size as compared to sol gel method.
3.2. DC electrical properties

The DC electrical resistivity of ferrites depends on grain size, chemical composition, density, porosity, sintering conditions etc [15, 16]. The variation in DC electrical resistivity as a function of temperature is shown in Fig. 2. The decrease in resistivity with temperature confirms the semiconducting nature of ferrites. The values of resistivity varies from $3.3 \times 10^{10}$ to $2.2 \times 10^{11}$ (ohm-cm) and $7.13 \times 10^{8}$ to $1.44 \times 10^{10}$ at $373$ K for sol gel and coprecipitation method respectively. These high values of resistivity at room temperature show that ferrites are insulators at room temperature. The variation in resistivity with Cd content is consistent with the results reported by Venkataraju et al [10]. According to Verwey and de Boer [17, 18] electron exchange take place between the ions of same element present in more than one valence state and distributed randomly over crystallographic lattice sites.
The decrease in DC electrical resistivity with increase in temperature is due to increased drift mobility of the charge carriers. The electrons hopping energy in ferrites is responsible for conduction mechanism depends on the activation energy and is associated with electrical energy barrier during electron hopping [19]. The activation energies are calculated from slope of resistivity plots. The value of activation energy increased with the addition of Cd$^{2+}$ ions for sol gel samples which suggests that the conduction mechanism in the present ferrite system is due to hopping of polarons.

3.3 Dielectric properties
3.3.1 Dielectric constant

The dielectric constant is represented in terms of real and imaginary parts as

$$e = e' - j e'' \quad (6)$$

The real part of dielectric constant gives the stored energy and imaginary part gives the dissipation of energy in applied ac field. The variation in dielectric constant ($e'$) with applied field of 1V/m in the frequency range from 20 Hz to 5 MHz, for all compositions is shown in Fig. 3. The dielectric constant decreases with increase in frequency for all compositions. This decrease is rapid at lower frequency region and slows down at high frequency.

![Fig. 3 Variation in (a) dielectric constant and (inset) dielectric loss factor ($D$) with frequency up to 5 MHz for Mn$_{0.5}$Zn$_{0.5-x}$Cd$_x$Fe$_2$O$_4$ nano ferrites.](image)

The dispersion in dielectric constant is due to Maxwell-Wagner [20] type interfacial polarization, which agrees with the Koop’s phenomenological theory. The large values of $e'$ at lower frequency are due to predominance of species like Co$^{2+}$, Fe$^{2+}$ ions, oxygen vacancies, grain boundary defects, interfacial distribution, etc. [6, 21]. The process of polarization in ferrites is similar to the conduction mechanism [22]. The transfer of electron between Fe$^{2+}$ (ferrous ions) and Fe$^{3+}$ (ferric ions) and holes between Mn$^{3+}$ and Mn$^{2+}$ ions leads the displacement of electrons in the direction of applied field and hence cause the polarization. This type of behavior is reported earlier for Mn-Zn-Cu [23] and Ni-Co [15] systems. At high frequency polarization decreases and reaches a constant value due to the fact that after certain frequency of the applied field the electron hopping does not follow the alternating field. The slight decrease in the dielectric values between 1 MHz to 1 GHz is represented in Fig. 4. Table 2 shows that the value of dielectric constant is minimum for $x = 0.25$ concentration of Cd$^{2+}$ ions in both types of samples.
3.3.2 Dielectric Loss tangent

The energy dissipation in the dielectric system is represented by the dielectric loss factor \((D)\) or loss tangent \((\tan \delta)\). The domain wall resonance is considered to be the cause of this loss. These losses are low at high frequency due to hindrance in the domain wall rotation. The dielectric loss factor is proportional to the imaginary part of dielectric constant according to Eq. (3). The variation in dielectric loss factor \((D)\) with applied frequency at room temperature for \(\text{Mn}_{0.5}\text{Zn}_{0.5-x}\text{Cd}_x\text{Fe}_2\text{O}_4\) \((x = 0, 0.15, 0.25, 0.35)\) composition is shown in the inset of Fig. 3. The dielectric loss factor increased with frequency up to a maximum value and then starts decreasing with increase in frequency. The appearance of these loss peaks for the sol-gel prepared samples shows the relaxation process occurred with the change in frequency in the polycrystalline Mn-Zn soft ferrites. The samples prepared by coprecipitation method gives no such peak.

Table 2 Dielectric constant \((\varepsilon)\) and dielectric loss factor \((D)\) of the \(\text{Mn}_{0.5}\text{Zn}_{0.5-x}\text{Cd}_x\text{Fe}_2\text{O}_4\) nano ferrites with varying \(\text{Cd}^{2+}\) ions concentrations \(0 \leq x \leq 0.35\) prepared by sol gel and coprecipitation methods.

| Composition    | \(x = 0\) | \(x = 0.15\) | \(x = 0.25\) | \(x = 0.35\) |
|---------------|-----------|--------------|--------------|--------------|
| \(\varepsilon\) at 1 kHz | 620       | 98           | 33           | 116          |
| \(\varepsilon\) at 1 MHz  | 20        | 24           | 21           | 32           |
| \(\varepsilon\) at 1 GHz  | 8.61      | 11.81        | 4.06         | 7.22         |
| \(\tan \delta\) at 1 kHz | 2.50      | 8.38         | 1.79         | 9.94         |
| \(\tan \delta\) at 1 MHz  | 0.17      | 0.30         | 0.12         | 0.26         |
| \(\tan \delta\) at 1 GHz  | 0.14      | 0.027        | 0.022        | 0.018        |

Coprecipitation

| Composition    | \(x = 0\) | \(x = 0.15\) | \(x = 0.25\) | \(x = 0.35\) |
|---------------|-----------|--------------|--------------|--------------|
| \(\varepsilon\) at 1 kHz | 24962     | 101          | 64           | 188          |
| \(\varepsilon\) at 1 MHz  | 904       | 33           | 27           | 30           |
| \(\varepsilon\) at 1 GHz  | 50        | 7.68         | 10.36        | 8.33         |
| \(\tan \delta\) at 1 kHz | 1.53      | 0.46         | 0.21         | 0.98         |
| \(\tan \delta\) at 1 MHz  | 1.9       | 0.24         | 0.17         | 0.19         |
| \(\tan \delta\) at 1 GHz  | 0.45      | 0.01         | 0.009        | 0.006        |

The peak formed when the jumping frequency of charge carriers approximately becomes equal to external applied ac field [14]. The relaxation phenomenon also occurred in 1 MHz to 1 GHz range for sol-gel prepared samples (see inset of Fig. 3). The dielectric loss is also minimum for the concentration of \(\text{Cd}^{2+}\) at \(x = 0.25\) given in Table 2 \((1.79 \text{ at 1 kHz and 0.12 at 1MHz})\). It is known that \(\text{Zn}^{2+}\) ions occupy the tetrahedral A-site and \(\text{Mn}^{2+}\) and \(\text{Fe}^{3+}\) ions have tendency to occupy both A and B-sites [24]. It is reported that \(\text{Cd}^{2+}\) ions occupy A-site [25]. The substitution on of \(\text{Cd}^{2+}\) ions increases the resistivity of the Mn-Zn ferrites. The dielectric behavior is directly proportional to the square root of conductivity that is why both dielectric constant and loss tangent decreased with cadmium concentration. Similar results are reported by Hankare et al. [26] for Cr substituted Mn-Zn ferrites.
Figure 4. Variation in the dielectric constant and dielectric loss factor with frequency up to 1GHz for Mn$_{0.5}$Zn$_{0.5-x}$Cd$_x$Fe$_2$O$_4$ nano ferrites.

3.3.3 Impedance analysis

The impedance spectroscopy is widely used to characterize the electrical properties of materials and interfaces present in these materials. The impedance measurements data gives both resistive (real) and reactive (imaginary) components for a material. To separate the grain and grain boundary contributions of the Cd doped Mn-Zn ferrite samples, complex impedance plane plots (Cole-Cole plots) have been drawn in the frequency range from 20 Hz to 5 MHz at room temperature. It is clear from Fig. 5 that all the samples show single semicircle which is due to the conduction of the grains and one incomplete arc is due to grain boundary conduction, except for $x = 0.35$

Fig. 5 Cole-Cole plots for Mn$_{0.5}$Zn$_{0.5-x}$Cd$_x$Fe$_2$O$_4$ nano ferrites at room temperature.

The incomplete circular arc in low frequency region shows that grain boundary resistance is out of measurement scale or presence of some additional relaxation phenomena which occur outside the measured frequency range [27]. Grain resistance increases with Cd$^{2+}$ concentration which is in agreement with the electrical measurements.
4. Conclusions
The Cd substituted Mn-Zn nano ferrites with composition Mn$_{0.5}$Zn$_{0.5-x}$Cd$_x$Fe$_2$O$_4$ ($x = 0, 0.15, 0.25, 0.35$) have been prepared by the sol gel auto-combustion and coprecipitation methods. All the samples showed single phase FCC spinel structure. It is observed that the lattice constant, average crystallite size and XRD density increases with the Cd$^{2+}$ concentration in both types of samples. The DC electrical resistivity increased to maximum value of $2.2 \times 10^{11}$ (Ω-cm) (sol gel) and $1.44 \times 10^{10}$ (Ω-cm) (coprecipitation) for $x = 0.25$ concentration of cadmium. The dielectric constant found to be minimum for $x = 0.25$ of Cd$^{2+}$ doping in both types of samples. The presence of Debye peak in loss tangent vs frequency curves confirms the existence of single relaxation phenomena in the given frequency range for the sol gel prepared samples. The complex impedance plane plots show a single semicircle, which indicates the capacitive and resistive properties of the materials are due to contribution of grains and grain boundaries in ferrites. The substitution of Cd$^{2+}$ plays an important role to modify the electrical properties of Mn-Zn ferrites required for power applications and microwave devices.

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References
[1] Lim I I S et al 2008 Nanotechnology 19 305102
[2] Fontijn W F J et al 1997 Phys. Rev. B 56 5432
[3] Philip J et al 2008 Appl. Phys. Lett. 92 043108
[4] Li Q, Wang Y and Chang C. 2010 J. Alloys Comp. 505 523
[5] Veena E G et al 2010 Appl. Phys. A 99 497
[6] Farea A M M et al. 2008 J. Alloys Comp. 464 361
[7] Batoo K M, Kumar S, Lee C G and Alimudddin. 2009 Curr. Appl. Phys. 9 826
[8] Jacob B P, Thankachen S, Xavier S and Mohammed E M. 2011 Phys. Scr. 84 045702
[9] Nikumbh A K et al 2002 J. Mater. Sci. 37 634
[10] C. Venkataraaju, G.Sathishkumar and K.Sivakumar. 2011 J. Magn. Magn. Mater. 323 1817
[11] Pant R P, Kumar V, Haldar S K, Gupta S K and Sukhvir S. 2007 Int. J. Nanosci. 6 515
[12] Kumar V, Rana A, Yadav M S and Pant R P. 2008 J. Magn. Magn. Mater. 320 1729
[13] Gul I H, Abbasi A Z, Amin F, Rehman M A, and Maqsood A. 2007 J. Magn. Magn. Mater. 311 494
[14] Adeeben A M, Hemeda O M, Assem E E and El-Sehly M M. 2002 J. Magn. Magn. Mater. 238 75
[15] Gul I H, Ahmed W and Maqsood A. 2008 J. Magn. Magn. Mater. 320 270
[16] Magalaraja R V, Ananthakumar S, Manohar P and Gnanam F D. 2002 J. Magn. Magn. Mater. 253 56
[17] Verwey E J W. 1947 J. Chem. Phys. 24 174
[18] Verwey E J W and de Boer J H. 1936 Recl. Trav. Chim. Phys.- Bas 55 531
[19] Vijaya P, Bhasker R, Ramesh B and Gopal R C. 2010 Physica B: Condens. Matter. 405 1852
[20] Koop’s C G. 1951 Phys. Rev. 83 121
[21] Maxwell J C. 1973 Electricity and Magnetism, Vol 1. Oxford University Press, New York,
[22] Rabimkin L T and Novikova Z I. 1960 Ferrites, Acad. Naok, USSR, Minsk 146
[23] Harkare P P. et al 2011 J. Magn. Magn. Mater. 323 389
[24] Ajmal M and Maqsood A. 2008 Mater. Lett. 62 2077
[25] Ravinder D. 2000 J. Mater. Lett. 43 129
[26] Harkare P P, Patil R P, Garadkar K M, Sasikala R and Chougule B K 2011 Mater.Res.Bullet. 46 447
[27] Dar M A, Batoo K M, Verma V, Siddiqui W A and Kotnala R K. 2010 J. Alloys. Comp. 493 553