Mössbauer spectroscopic analysis and temperature dependent electrical study of Mg_{0.9}Mn_{0.1}Gd_{y}Fe_{2−y}O_{4} nanoferrites

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Mg–Gd–Mn nanoferrites with formulae Mg_{0.9}Mn_{0.1}Gd_{y}Fe_{2−y}O_{4} where y=0.05, 0.1, 0.2 and 0.3, have been synthesized by solution combustion technique. The dc resistivity was observed to decrease with the increase in temperature. Dielectric constant (ε’+ε”) and loss tangent (tan δ) have been found to be increasing with an increase in temperature while with an increase in frequency both have been found to be decreasing. The ac electrical conductivity (σ_ac) has been studied as a function of temperature at different frequencies and has been observed to be increasing with the increase in temperature. The Mössbauer spectroscopy has been carried out so as to authenticate our previously reported results on the superexchange interactions.

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1. Introduction

Ferrites are the ferromagnetic materials containing iron (III) oxide as their principal component. Ferrites are technologically important class of magnetic oxides due to their good magnetic properties, high electric resistivity, low eddy current loss and low dielectric loss [1]. The electric, dielectric and magnetic properties of ferrites can be tailored either by changing the microstructure or by incorporation of different metal ions [2,3]. Now-a-days, exploration of the nanosized ferrites is one of the most imperative and rapid growing area of research in the field of nanotechnology [4] to cope with the increased technological demand.

Mg–Mn ferrites are well known technological materials finding applications in various electrical and magnetic devices. The importance of Mg–Mn ferrites lies in their magnetic properties and low electrical conductivity which allow electromagnetic waves to propagate in the medium and make them suitable for applications in microwave devices. Mg–Mn ferrites are widely used in the construction of non-reciprocal devices at microwave frequencies such as circulators, gyrators and phase shifter. In addition to this, they are widely used in computer memory chips, magnetic recording media, and fabrication of radio frequency coils, transformers cores and rod antennas [5–7]. Due to the technological importance of Mg–Mn ferrites many researchers have investigated substituted Mg–Mn ferrites. Singh [8] has synthesized Mg_{x}Mn_{1−x}Fe_{2}O_{4} ferrites by conventional ceramic technique and the hot-pressed ceramic technique and then made a comparative study of electric and magnetic properties. Lakshman et al. [9] have synthesized the substituted Mg–Mn ferrites and reported the electric, dielectric and magnetic properties. Kumar et al. [10] have reported the effect of swift heavy ion irradiations on the magnetic properties of Mg–Mn ferrites. Okasha [11] reported the influence of gamma-irradiation on the structural and magnetic properties of Mg–Mn ferrites. Tsay et al. [12] have reported the effect of sintering temperature on the microstructural, magnetic and microwave properties of magnesium-manganese ferrites. Modi et al. [13] have reported the structural properties of co-precipitation synthesized Mg–Mn nanoferrites. Pathak et al. [14] have reported the study of Mg–Mn nanoferrites synthesized via co-precipitation method.

Although, there are reports on the dielectric and magnetic properties of mixed Mg–Mn ferrites but rarely any work has been reported on the Mössbauer and temperature dependent electrical properties of gadolinium substituted Mg–Mn nanoferrites prepared by solution combustion method. Therefore, in this paper, a maiden attempt has been made to investigate the temperature...
dependent electric, dielectric and ac conductivity behavior of Gd\(^{3+}\) substituted Mg–Mn nanoferrites synthesized by solution combustion method.

In past some researchers have reported the weakening of super-exchange interactions with the substitution of gadolinium content \([15–18]\), and many have claimed the increasing trend in the super-exchange interactions with the increasing content of Gd\(^{3+}\) ions \([19,20]\). Therefore, due to above mentioned results for Gd\(^{3+}\) substitution we aimed to understand the effect of Gd\(^{3+}\) ions on the exchange interactions in details. Recently, we had reported the detailed theoretical discussions along with experimental results regarding the effects on the super-exchange interactions with the substitution of Gd\(^{3+}\) ions in the Mg–Mn nanoferrite matrix \([21]\). Since, the Mössbauer spectroscopy is one of the important techniques which can measure the comparatively weak interactions between the nucleus and the surrounding electrons; therefore, in the present work we have carried out Mössbauer spectroscopy analysis so as to support our recently published results.

2. Experimental procedure

Mg\(_{0.9}\)Mn\(_{0.1}\)Gd\(_{y}\)Fe\(_{2–y}\)O\(_{4}\) nanoferrites, where \(y = 0.05, 0.1, 0.2\) and 0.3, have been prepared by the solution combustion technique. The chemical reagents used in the present work were ferric nitrate (Fe(NO\(_3\))\(_3\)·9H\(_2\)O), gadolinium nitrate (Gd(NO\(_3\))\(_2\)·9H\(_2\)O), magnesium nitrate (Mg(NO\(_3\))\(_2\)·6H\(_2\)O) and manganese nitrate (Mn(NO\(_3\))\(_2\)·4H\(_2\)O) and glycine (NH\(_2\)CH\(_2\)COOH) was used as a fuel. In a stoichiometric ratio all the above mentioned nitrates and glycine were dissolved in distilled water so as to obtain the precursor solution. The obtained precursor solution was then heated on a hot plate at 80 °C with a constant stirring till the solution starts to burn with liberation of lots of heat. The obtained powder samples were then calcined at 500 °C for 4 h. The calcined powders obtained for all the nanoferrites were then pressed into pellets of thickness 2 mm and diameter 10 mm under a pressure of 3–5 t/in\(^2\). The prepared samples were then sintered at 700 °C for 4 h. The single-phase nature of the prepared samples was investigated by the X-ray diffraction (XRD) study which was carried out with Cu-K\(_\alpha\) radiation of wavelength 1.54 Å using Rigaku-Denki X-ray diffractometer. The temperature dependence of dc resistivity of all the samples was studied with the help of Keithley instrument model 2611. The dielectric properties such as dielectric constant and dielectric loss have been investigated as a function of frequency in the range of 100 Hz to 1 MHz at different temperatures by using WAYNER KERR 6500 impedance analyzer. Mössbauer spectroscopy at room temperature was carried out by using a constant acceleration driven Mössbauer spectrometer model FAST Com Tec 070906. The experimental data is fitted with NORMOS (DIST) fitting package \([22]\) and the best fit is considered for minimum deviation (χ\(^2\)) between experimental and theoretical spectrum.

3. Results and discussion

3.1. Structural study

The X-ray patterns of Mg\(_{0.9}\)Mn\(_{0.1}\)Gd\(_{y}\)Fe\(_{2–y}\)O\(_{4}\), \(y = 0.05, 0.1, 0.2\) and 0.3, nanoferrites, which indicated a typical cubic spinel structure were published by our group in our previous publication \([21]\). It has been reported by Shirsath et al. \([23]\) that rare-earth doped ferrites show extra crystalline phases because of their low solubility and large ionic radii. The XRD patterns obtained for the
present samples indicated that no unreacted constituents were present in the samples. The calculated values of particle size were observed to be 13.4 nm, 14.6 nm, 15.2 nm and 16.1 nm for $y = 0.05, 0.1, 0.2$ and $0.3$ respectively. The detailed structural analysis is presented by the author elsewhere [21].

3.2. Variation of dc resistivity with temperature

Fig. 1 shows the variation in dc resistivity as a function of temperature for all the synthesized nanoferrites. The dc resistivity is observed to be decreasing with an increase in temperature, i.e. exhibiting semiconducting behavior [24], according to the well known Arrhenius equation [25]:

$$\rho = \rho_0 \exp \frac{\Delta E}{kT}$$  \hspace{1cm} (1)

where $\Delta E$ is activation energy, which is the energy needed to release an electron from the ion for a jump to the neighboring ion, thus giving rise to electrical conductivity, $\rho_0$ is pre-exponential factor, $k$ is Boltzmann constant, $T$ is absolute temperature. The resistivity decrease with an increase in temperature because an increase in temperature will enhance the drift mobility of the charge carriers; since rise in temperature will help the bound charges to participate in the conduction process [26]. The calculated values of activation energy are given in Table 1. It is evident to Table 1 that ferrimagnetic region has lower activation energy values as compared to the paramagnetic region. The lower activation energy in the ferrimagnetic region is attributed to the magnetic disordering [27] due to the decrease in concentration of current carriers [28], while the change in activation energy is attributed to the change in conduction mechanism [29,30]. The change in activation energy for different compositions is attributed to the hoping of polarons. The values of activation energy above 0.2 eV clearly indicate the polaron hopping in the synthesized nanoferrites [31]. Further, from Fig. 2, it is evident that the dc resistivity is increasing with an increasing substitution of Gd$^{3+}$ ions. In ferrites, the Fe$^{3+}$ ions are moderately reduced to Fe$^{2+}$ ions during sintering of ferrites, which results in the formation of a small amount of Fe$^{2+}$ ions in these samples [32]. Also, a small fraction of Mn$^{2+}$ ions reacts with Fe$^{3+}$ ions to form Mn$^{3+}$ and Fe$^{2+}$ as per the following reaction:

$$\text{Mn}^{2+} + \text{Fe}^{3+} \rightarrow \text{Mn}^{3+} + \text{Fe}^{2+}$$  \hspace{1cm} (2)

The presence of Fe$^{2+}$–Fe$^{3+}$ and Mn$^{2+}$–Mn$^{3+}$ ion pairs of the same element but of different valences present at the equivalent crystallographic sites are responsible for conduction due to hopping of electrons in $\text{Mg}_{0.9}\text{Mn}_{0.1}\text{Fe}_{2-y}\text{O}_4$ ferrites [33]. Since Gd$^{3+}$ ions have a tendency to occupy octahedral sites, therefore, the addition of Gd$^{3+}$ ions in Mg–Mn ferrites will directly reduce the number of B-site Fe$^{3+}$ ions thus, limits the degree of conduction by blocking the Verwey’s hopping mechanism [34] resulting an increase in resistivity.

3.3. Variation of dielectric constant with temperature

The value of dielectric constant was calculated by using the following relation [34]:

$$\ln \sigma = \frac{-\Delta E}{kT} + \ln \sigma_0$$

Fig. 3. Variation of dielectric loss with temperature at different frequencies for $\text{Mg}_{0.9}\text{Mn}_{0.1}\text{Gd}_{y}\text{Fe}_{2-y}\text{O}_4$ nanoferrites.

Fig. 4. Variation of ac conductivity with frequency at different temperatures for $\text{Mg}_{0.9}\text{Mn}_{0.1}\text{Gd}_{y}\text{Fe}_{2-y}\text{O}_4$ nanoferrites.
The dielectric constant ($\varepsilon'$) of the materials is observed to be increasing slowly with an increase in temperature while at higher temperature (beyond 650 K) it is increasing rapidly. As these variations are similar to dielectric constant therefore can be explained in a similar way. The energy losses in the dielectrics are because of the electric conductivity of the materials and the relaxation effect to the orientation of the dipole. The increase in the dielectric loss tangent with an increase in temperature is suggesting that with an increase in temperature, the losses due to dipole orientations are decreasing while the losses due to electric conductivity are increasing. Further, it is also evident from the results that at all temperatures the dielectric loss tangent is decreasing with the increase in frequency. These results are in close agreement with Koop’s phenomenological model [37]. Generally, the dielectric loss comes up when the polarization lags behind the applied alternating field and is originate because of the existence of impurities and structural inhomogeneities. Thus, the low values of dielectric loss tangent achieved in the present work are therefore attributed to more structurally perfect and homogeneous nano ferrites synthesized by the solution combustion technique.

3.4. Variations of dielectric loss with temperature

Fig. 3 shows the variations of dielectric loss tangent ($\tan \delta$) as a function of temperature at different frequencies. It is evident from results that the dielectric loss tangent is increasing slowly with an increase in temperature while at higher temperature (beyond 650 K) it is increasing rapidly. As these variations are similar to dielectric constant therefore can be explained in a similar way. The energy losses in the dielectrics are because of the electric conductivity of the materials and the relaxation effect to the orientation of the dipole. The increase in the dielectric loss tangent with an increase in temperature is suggesting that with an increase in temperature, the losses due to dipole orientations are decreasing while the losses due to electric conductivity are increasing. Further, it is also evident from the results that at all temperatures the dielectric loss tangent is decreasing with the increase in frequency. These results are in close agreement with Koop’s phenomenological model [37]. Generally, the dielectric loss comes up when the polarization lags behind the applied alternating field and is originate because of the existence of impurities and structural inhomogeneities. Thus, the low values of dielectric loss tangent achieved in the present work are therefore attributed to more structurally perfect and homogeneous nano ferrites synthesized by the solution combustion technique.

3.5. Variation of ac conductivity

The ac conductivity ($\sigma_{ac}$) is calculated from dielectric data using following relation [22]:

$$\sigma_{ac} = \varepsilon' \varepsilon_0 \omega \tan \delta$$

where $\varepsilon'$ is dielectric constant, $\varepsilon_0$ is permittivity of free space, $\omega$ is angular frequency. Fig. 4 shows the variations of ac conductivity as a function of frequency at different temperatures. The plots for variations of ac electrical conductivity with frequency are observed to be almost linear confirming the polaron type conduction. The observed variation of ac conductivity as a function of frequency can be enlighten in view of Maxwell–Wagner heterogeneous model [35,36] of the polycrystalline structure of ferrites. In this model, the dielectric structure is divided into two layers. The first layer consists of well conducting ferrite grains which is separated by a second thin layer of weakly conducting substances termed as grain boundary. At lower frequencies these grain boundaries are more active due to which the hopping frequency of electron between Fe$^{3+}$ and Fe$^{2+}$ is less at lower frequencies. As the frequency of an applied field increases, the conductive grains become more active by encouraging the hopping of electron between Fe$^{3+}$ and Fe$^{2+}$ ions resulting thereby gradual increase in ac conductivity with frequency. Fig. 5 shows the variations of ac conductivity as a function of temperature at different frequencies. It is observed that the conductivity is increasing with the increase in temperature and is due to the thermally enhanced drift mobility of charge carriers. Further it is evident from the results that at high temperatures the
conductivity became almost frequency independent. This is because of the facts that at high temperature region the frequency independent part dominate; hence, the frequency dependence of ac conductivity becomes less significant.

3.6. Mössbauer spectroscopy analysis

Fig. 6 shows the room temperature Mössbauer spectra for Mg$_{0.9}$Mn$_{0.1}$Gd$_y$Fe$_2$O$_4$ ($y = 0.05, 0.1, 0.2, 0.3$) nanoferrites. The experimental data is fitted with NORMOS (DIST) program. The average values of hyperfine field and isomer shift are listed in Table 2. The isomer shift (IS) arises due to the electrostatic interaction between the charge distribution of the nucleus and those electrons that have a finite probability of being found in the region of the nucleus. Only s-electron wave functions have a finite value at the nucleus and these electrons are, therefore, responsible for this interaction. The isomer shift is a physical parameter for probing the valence state of a Mössbauer atom. It can be concluded from Table 2 that the observed value of average isomer shift is consistent with the presence of iron in $3^+$ state. The splitting in the Mössbauer spectrum which originates because of the coupling between the nuclear magnetic moment and the magnetic field at the nucleus is called hyperfine interaction or Zeeman splitting. In general, the magnetic field can originate either within the atom itself, within the crystal via exchange interactions and from applied external field. The Hamiltonian for the interaction can be expressed as:

$$H_I = -\mu N \cdot I \cdot H$$

where $N$ is the nuclear Bohr magneton, $\mu$ is nuclear magnetic moment, $I$ is the nuclear spin and $g$ is the gyromagnetic ratio. The eigen values of Hamiltonian can be expressed as:

$$E_m = -\mu H m I$$

where $m$ ($m = +I, I-1, I-2, \ldots \ldots -I$) is the magnetic quantum number representing the Z-component of $I$. The magnetic field therefore splits a nuclear spin $I$ into $2I+1$ sublevels. A Mössbauer transition can take place if the change in the $m$ value is $0$ or $\pm 1$. So in case of $^{57}$Fe, the excited level $I=3/2$ splits into 4 sublevels and $I=1/2$ ground state splits into 2 sublevels, giving six Mössbauer transitions between these sublevels i.e sextet. The fluctuation of magnetization vectors in a direction close to an easy direction of magnetization leads to a particle size dependent magnetic hyperfine field. If the correlation time of the collective magnetization fluctuations is short relative to the observation time, the measured value of the magnetic field and consequently the hyperfine field will be reduced according to the equation:

$$H_m = -g_H H I$$

Table 2
Mössbauer parameters: average hyperfine field (HF), and average isomer shift (IS) of Mg$_{0.9}$Mn$_{0.1}$Gd$_y$Fe$_2$O$_4$ nanoferrites.

<table>
<thead>
<tr>
<th>$y$</th>
<th>HF field (T)</th>
<th>IS (mm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>39.20</td>
<td>0.58</td>
</tr>
<tr>
<td>0.1</td>
<td>33.95</td>
<td>0.50</td>
</tr>
<tr>
<td>0.2</td>
<td>31.60</td>
<td>0.52</td>
</tr>
<tr>
<td>0.3</td>
<td>30.84</td>
<td>0.524</td>
</tr>
</tbody>
</table>

Fig. 6. Room temperature Mössbauer spectra for Mg$_{0.9}$Mn$_{0.1}$Gd$_y$Fe$_2$O$_4$ nanoferrites.
where $k_B$ is the Boltzmann’s constant, $V$ is the particle volume and $V \rightarrow \infty$, refers to a large crystals at temperature $T$ in the absence of collective magnetic excitations. Therefore, according to Eq. (8) the hyperfine filed decreases with the decrease in particle size since particles with different volumes will show different hyperfine splitting. It can be seen from Fig. 6 that with the substitution of Gd$^{3+}$ ions there are doublets in place of well defined sextets which indicates that incorporation of Gd$^{3+}$ ions in the Mg–Mn nanoferrite matrix is making the system more non ferromagnetic. Further, it can be observed from Table 2 that average magnetic hyperfine field (HF) is decreasing with the increasing content of gadolinium ions in the Mg–Mn nanoferrite matrix irrespective of the fact that particle size is increasing with the increasing substitution of Gd$^{3+}$ ions. The observed variations in the magnetic hyperfine field show that the increasing content of gadolinium ions is weakening the A–B super-exchange interactions. Peng et al. [15] and Iqbal et al. [16] reported that the magnetic moments of the rare-earth ions usually originate from the localized 4f electrons; at room temperature, their magnetic dipolar orientation is disordered. In addition to this, Iqbal et al. [16] and Jing et al. [17] claimed that at room temperature, Gd$^{3+}$ ions are non-magnetic ions having no contribution to the magnetization of doped ferrite. Since the magnetic moment of each composition depends on the magnetic moments of engaged ions, therefore, Neills et al. [18] also reported that magnetic moments of rare-earth ions are characterized by lower magnetic ordering temperatures, i.e. lower than 40 K and their magnetic dipolar orientation is disordered at room temperature. So again they considered Gd$^{3+}$ ions as non-magnetic ions, which make no contribution to the magnetization of doped ferrite at room temperature. Therefore, in view of the above reported papers [15–18,38–40], it can be concluded that apart from increasing trend of particle size, the non-magnetic contribution of the Gd$^{3+}$ ions is resulting in doublets as well as is also responsible for the decreasing behavior of hyperfine field. The observed variations in the magnetic hyperfine field show that the increasing content of gadolinium ions is weakening the A–B super-exchange interactions and the same is in agreement with our recently published work [21]..

4. Conclusions

Gadolinium substituted Mg–Mn nanoferrites were successfully processed by solution combustion technique. The dc resistivity is observed to be decreasing with an increase in temperature. Dielectric constant, loss tangent, and ac conductivity are observed to increase with an increase in temperature. Room temperature Mössbauer spectra of the synthesized nanoferrites showed an increase in the paramagnetic doublet with the increasing substitution of Gd$^{3+}$ ions. The magnetic hyperfine field was observed to be decreasing with the increasing content of gadolinium ions. Therefore, suggesting that the increasing content of gadolinium ions is weakening the A–B exchange interactions. The very high values of dielectric constant and the low values of dielectric loss tangent are obtained in the present work which makes these nanoferrites very suitable for microwave applications.

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