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Study of electric and dielectric properties of In^{3+} and Al^{3+} substituted Mg-Mn ferrites synthesized by citrate precursor method

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ABSTRACT

Mixed Mg-Mn ferrites of compositions $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ and $Mg_{0.9}Mn_{0.1}Al_yFe_{2-y}O_4$ have been synthesized by the citrate precursor technique. The X-ray diffraction patterns of the samples confirmed the formation of single-phase spinel structure. The ferrites have been investigated for their electric and dielectric properties. The dc resistivity and Curie temperature were found to be increasing with the increase in cobalt content. The mechanisms contributing to these results are discussed minutely in this paper. *PACS:* 75.50. Gg.

***Keywords**:* Mg-Mn ferrite; Citrate precursor technique; dc resistivity; dielectric constant; dielectric loss

INTRODUCTION

Spinel ferrites are studied extensively because they play a vital role in the technological applications [1-3]. The Mg-Mn ferrites are quite versatile from the point of view of their application and simplicity of their preparation. Properties of ferrites are known to be sensitive to their composition and the processing technique used to synthesize them [4]. A small deviation in the compositional stoichiometry of the ferrite affects its properties greatly [5]. Mg-Mn ferrites, synthesized by conventional techniques, were studied by so many workers [6-7], but, a very little literature is available on the study of these ferrites by non-conventional method. The conventional process is known to have some inherent drawbacks such as poor compositional control, chemical inhomogeneity, introduction of various impurities during the ball-milling [8]. Therefore, in the present study, non-conventional technique known as citrate precursor method [9-10] is employed for the preparation of ferrite series. This method does not require any ball milling to mix the materials as required in the conventional method, so, there is no possibility of impurity and hence of non-stoichiometry. Although the magnetic properties of Mg-Mn ferrites have been studied extensively [11-12] yet literature on the electric properties is scarce. The dc resistivity of ferrites is an important property, since it determines their performance at high frequencies, where eddy current losses may be high, resulting in a significant loss of energy and also ferrites having extremely low dielectric loss are very useful for microwave communication. Thus, in the present investigation, we concentrate on the study of the electric and dielectric properties such as resistivity, dielectric constant and dielectric loss of In^{3+} and Al^{3+} doped Mg-Mn ferrite series.

EXPERIMENTAL PROCEDURE

The ferrite series with the composition $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ (S1 for x = 0.1 & S2 for x=0.2) and $Mg_{0.9}Mn_{0.1}Al_yFe_{2-y}O_4$(S3 for y=0.1,S4 for y=0.5 &S5 for y= 0.7) were prepared by using hydrated nitrates of the constituent elements of purity ≥ 98%. The chemicals used were as:
(a) $Mg(NO_3)_2.6H_2O$, (b) $Mn(NO_3)_2.4H_2O$, (c) $Al(NO_3)_3.9H_2O$, (d) $In(NO_3)_3.5H_2O$ and (e) Iron was in the form of iron citrate $C_6H_5O_7Fe.3H_2O$. The solid state reactions used for the preparation of the samples were as:

(1)$0.9[Mg(NO_3)_2.6H_2O]+0.1[Mn(NO_3)_2.4H_2O]+x[In(NO_3)_3.5H_2O]+(2-x)[C_6H_5O_7Fe.\ 3H_2O] \rightarrow [Mg_{0.9}\ Mn_{0.1}\ In_x\ Fe_{2-x}\ O_4]$

(2)$0.9[Mg(NO_3)_2.6H_2O]+0.1[Mn(NO_3)_2.4H_2O]+y[Al(NO_3)_3.9H_2O]+(2-y)[C_6H_5O_7Fe.\ 3H_2O] \rightarrow [Mg_{0.9}\ Mn_{0.1}\ Al_y\ Fe_{2-y}\ O_4]$

The quantities of the reagents required for each composition were calculated from the above solid state reactions. The experimental details are discussed by the author elsewhere [13]. The temperature dependence of dc resistivity of all the samples was studied using two probe methods. The single- phase nature of the prepared samples was checked by X-ray diffraction studies, which were made by Riga Ku Geiger Flex 3 kW diffractometer and the microstructures of the fractured surfaces of the samples were studied using a Cambridge Stereo Scan 360 scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Structural study

XRD pattern of S1 & S3 ferrite samples sintered at 1200^0C are shown in Fig.1. The observed diffraction lines were found to correspond to those of standard pattern of Mg-Mn ferrite with no extra lines, indicating thereby the single phase cubic spinel structure of the sample with no unreacted constituent. In order to confirm the homogeneity of the samples scanning electron micrographs were taken. Fig. 2 shows typical SEM for ferrite compositions S1 & S3. The particles are very small, on average ~0.5 µm.

Electrical resistivity and activation energy

The variation of resistivity as a function of temperature is shown in Figure 3. The change in slope is markedly observed in all the samples, such change is either due to Curie temperature [14] or due to change in conduction mechanism [15]. This indicates the semiconducting nature of ferrites. The resistivity of the samples decreases with the increase in temperature according to the relation

$$\rho = \rho_o \exp (E_\rho / kT) \qquad \dots (1)$$

where E_ρ is activation energy [16] which is the energy needed to release an electron from the ion for a jump to the neighbouring ion, so giving rise to electrical conductivity, k is Boltzmann constant & T is Absolute temperature. Each sample shows a break near the Curie temperature which is attributed to the transition from ferri to paramagnetic region. The activation energies are calculated from the slopes of the paramagnetic and ferromagnetic region according to the relation [17]

$$E_\rho = [0.198 \times 10^{-3} \times d\ (\log \rho)]/d(1/T)$$

The calculated values are given in Table 1 along with Curie temperature. From Table it is evident that the value of activation energy in the ferromagnetic region is lower than that of the paramagnetic region. The lower activation energy in the ferromagnetic region is attributed to the magnetic disordering [18] due to the due to the decrease in concentration of current carriers [19], while the change in activation energy is attributed to the change in conduction mechanism [20-21]. 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 system [22]. Further, resistivity was found to be increasing with the increasing substitution of In^{3+} and Al^{3+} ions. Kirichok and Antoshchuk [23] have shown that In^{3+} ions have strong preference to occupy tetrahedral site, it would dilute the conduction mechanism at the tetrahedral site. The addition of non magnetic Al^{3+} ions in place of Fe^{3+} ions limits the degree of conduction by blocking the Verway hopping mechanism [24], which results an increase in resistivity. The increase of the electrical resistivity for the investigated system gives a promising property for communication systems as the eddy current loss decreases.

Dielectric constant

Fig.4. shows the frequency variation of dielectric constant for In^{3+} and Al^{3+} doped Mg-Mn ferrite series. The dielectric constant decreases with increase of frequency for all samples. The observed observations for the samples show typical dispersion curves, which result from space charge polarization due to

inhomogeneous dielectric structure as pointed out by Wagner [25]. All the samples exhibit dispersion due to Maxwell [26] interfacial polarization in agreement with Koop's phenomenological theory [27]. It can be seen in the dielectric constant initially decreases rapidly with increasing frequency and thereafter it remains constant above 1 kHz for all the samples. The decrease of dielectric constant with increasing frequency is due to lag of hopping frequency of electrons between Fe^{2+} and Fe^{3+} ions against the frequency of external applied a.c. field and beyond a certain limit of external field, it becomes independent of it. Workers [28-30] who studied the variation of dielectric constant with frequency at low enough frequencies (100Hz-1000Hz) have indeed observed a constancy of dielectric constant with frequency, consistent with Koop's model. So the samples studied in the present work are consistent with Koop's model. The low value of dielectric constant is attributed to the method of preparation as citrate precursor method suppresses the formation of Fe^{2+} ions.

Fig.5 shows the temperature dependence of dielectric constant at 1 kHz for all the compositions. The dielectric constant increases very slowly up to ~500 K and after that it increases rapidly with increasing temperature for all the compositions. The slow increase in the dielectric constant may be due to space charge polarization caused by the conduction in these materials below 500 K by small impurities or interstitials. Above temperature T~500 K, dielectric constant for all the compositions increases rapidly. The rapid increase of dielectric constant may be understood as the combined effect of the two factors, namely space charge polarization and interfacial polarization. If these charges are some how not able to discharge at electrodes, an interfacial type of polarization results leading to a large increase in dielectric constant. The number of charge carriers increases exponentially and they produce space charge and interfacial polarization due to increase in temperature. This leads to a rapid increase in dielectric constant in the narrow band semiconductors, the charge carriers are not able to move freely with the electric field. If these charges are trapped, a space charge polarization builds up. The trapping or localisation of the charge carriers also increases the dielectric constant. As the temperature increases, the probability of their being localized becomes high to distortion of band by potential fluctuation. Due to these factors, the dielectric constant increases rapidly with increase in temperature. This behaviour was observed by many workers [31-34].

Dielectric loss

The plot of dielectric loss tangent (tan δ) versus log frequency at room temperature is shown in Fig. 6. All the samples show a normal dielectric behaviour with frequency. The dielectric loss in case of substituted Mg-Mn ferrites prepared by citrate precursor method is two or three orders of magnitude less as compared to Mg-Mn ferrites prepared by conventional ceramic method [35]. The lower values of dielectric loss tangent are result of appropriate control of chemical composition and improved microstructure of ferrites prepared by citrate precursor method [36]. The other reason for low dielectric loss is the higher value of restivity. The restivity of substituted Mg-Mn ferrites prepared by conventional method ranges from 10^5 Ω-cm to 10^{11} Ω-cm where as the restivity obtained for such ferrites prepared by citrate precursor method varies from 10^8 Ω-cm to 10^{15} Ω-cm. consequently if resistivity (ρ) increases the dielectric loss (P_e) is lowered in accordance with the well known relation [37];

$$P_e = (KB^2f^2d^2) / \rho \qquad \ldots(3)$$

Further, from Fig. 6, it is observed that dielectric loss is reduced with increased substitution in accordance with the relation (3). It is observed that the dielectric loss decreases exponentially with the increase of frequency and attains nearly constant value at higher frequencies.

Fig. 7 shows the variation of dielectric loss tangent with temperature for all the samples of the series at a constant frequency 1 kHz. It is observed that the dielectric loss tangent increasing with the increase in temperature. This behaviour of variation of dielectric loss tangent with temperature is in agreement with those reported by others [38]. The energy losses in the dielectrics are due to the electric conductivity of the materials and the relaxation effect to the dipole orientation. With temperature, losses due to dipole orientations decrease, while those due to electric conductivity increase. Since in the present work an increase in the dielectric loss is observed with temperature, it follows that losses due to electrical conductivity dominate over those due to relaxation effects.

CONCLUSIONS

The present study shows that with the citrate precursor technique we can process the ferrites at relatively lower temperatures, thus, due to lower processing temperature we have more uniform grain growth and atomic scale mixing at earlier stage of preparation of ferrite samples result in perfect crystal growth. As compositional stoichiometry plays a crucial role in modifying the ferrite properties, so, citrate precursor technique could be especially advantageous in processing ferrites for high frequency applications.

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Table 1 Activation energies and Curie temperature

Composition	Activation Energy (eV)			T_c (K) (From resistivity)
	E_f	E_p	E_ρ	
x,y=0.0	0.02	0.73	0.71	648
x=0.1	0.33	0.80	0.47	603
x=0.2	0.32	0.91	0.59	553
x=0.3	0.34	0.95	0.61	548
y=0.1	0.42	0.74	0.32	633
y=0.3	0.30	0.67	0.37	525
y=0.5	0.23	0.66	0.43	412

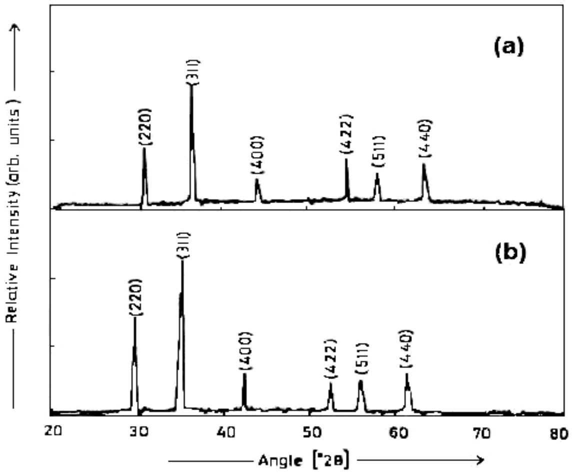

Fig.1. X-ray patterns of (a) $Mg_{0.9}Mn_{0.1}In_{0.1}Fe_{1.9}O_4$ and (b) $Mg_{0.9}Mn_{0.1}Al_{0.1}Fe_{1.9}O_4$ ferrite powders sintered at 1200^0C

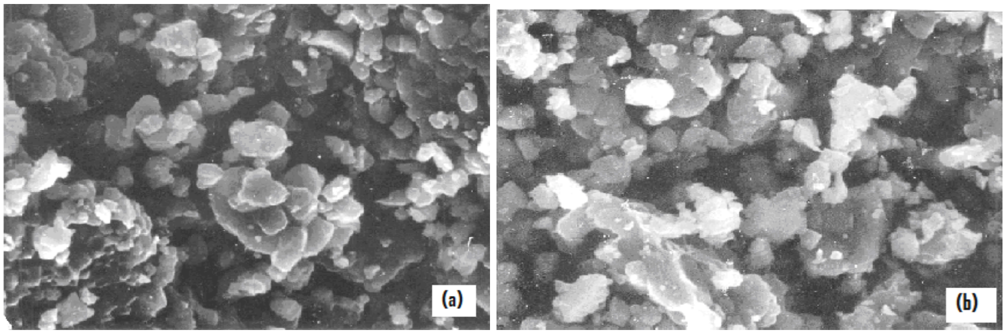

Fig.2. Scanning electron micrographs (SEM) of fractured surfaces for (a) $Mg_{0.9}Mn_{0.1}In_{0.1}Fe_{1.9}O_4$ and (b) $Mg_{0.9}Mn_{0.1}Al_{0.1}Fe_{1.9}O_4$ ferrites sintered at 1200^0C

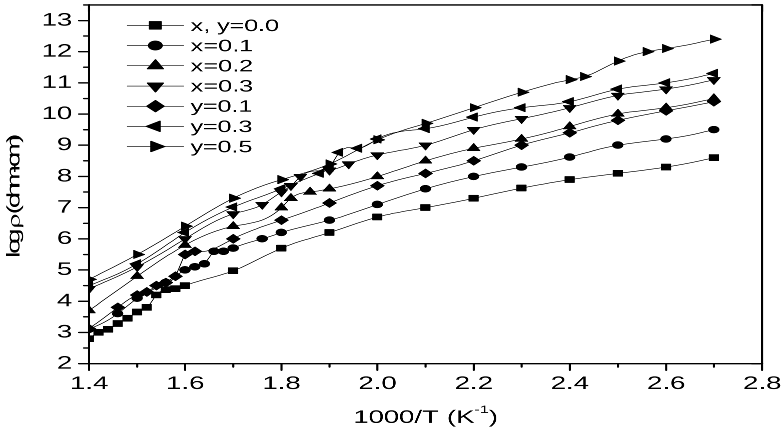

Fig.3. Variation of resistivity with temperature for $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ and $Mg_{0.9}Mn_{0.1}Al_yFe_{2-y}O_4$ ferrites

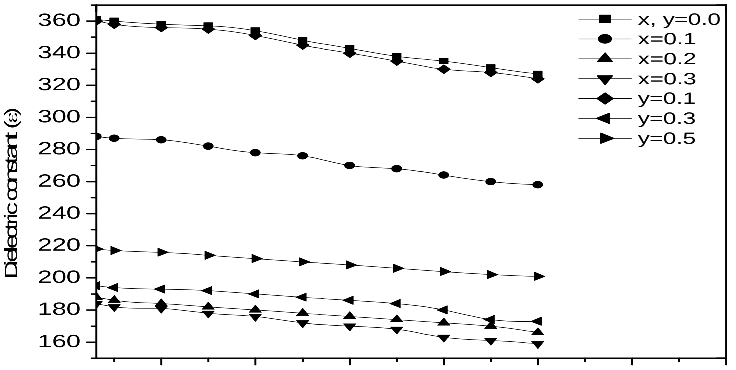

Fig.4 Variation of dielectric constant with frequency for $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ and $Mg_{0.9}Mn_{0.1}Al_yFe_{2-y}O_4$ ferrites

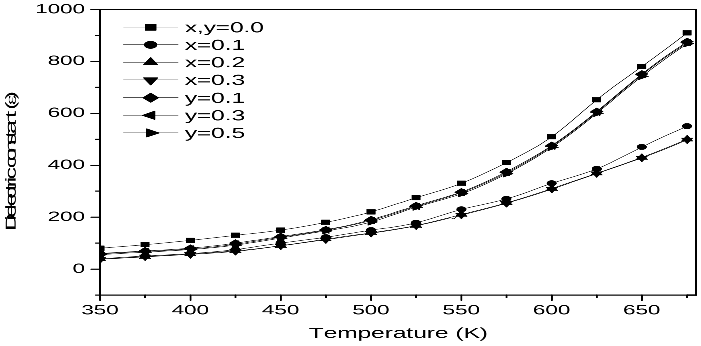

Fig.5 Variation of dielectric constant with temperature for $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ and $Mg_{0.9}Mn_{0.1}Al_yFe_{2-y}O_4$ ferrites at 1kHz.

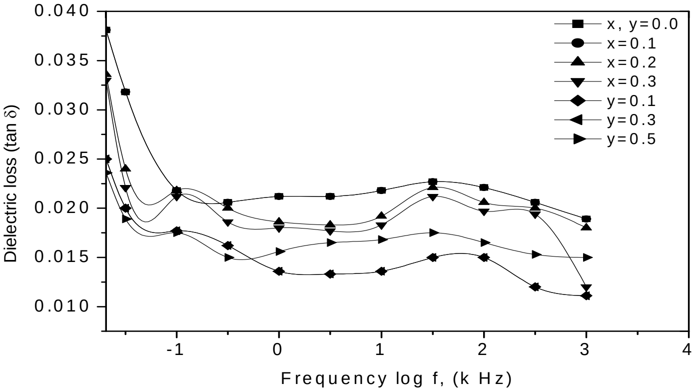

Fig.6 Variation of dielectric loss with frequency for $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ and $Mg_{0.9}Mn_{0.1}Al_yFe_{2-y}O_4$ ferrites

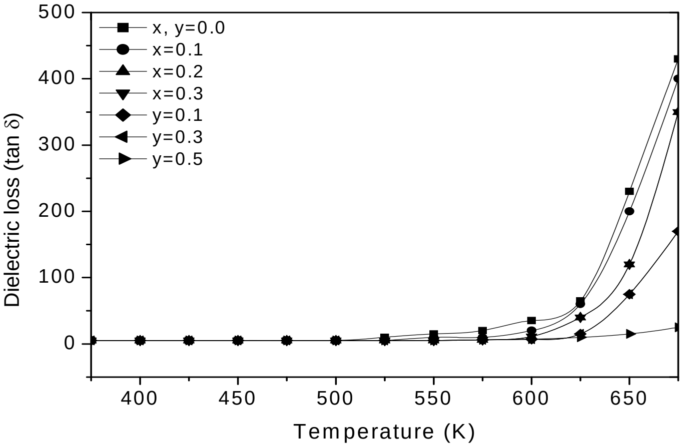

Fig.7 Variation of dielectric loss with temperature for $Mg_{0.9}Mn_{0.1}In_xFe_{2-x}O_4$ and $Mg_{0.9}Mn_{0.1}Al_yFe_{2-y}O_4$ ferrites at 1 kHz