Influence of rare earth substitution on thermo-electric power of Mg-Zn mixed ferrite

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ABSTRACT

Magnesium-Zinc ferrite substituted with rare earth ion Gd^{3+} with y = 0.05 and 0.10 are investigated. X-ray diffraction, IR absorption study of these compositions revealed the formation of single phase spinels. The temperature dependence of Thermo-electric power (TEP) is measured and then mobility of each sample calculated. The values of TEP (α) show n type conductivity suggesting the mechanism of conduction to be predominantly by electron hoping. On substitution of Gd^{3+} ion, TEP decreases which is assigned to the decrease of population of Fe^{3+} ions at the octahedral B site.

Keywords: Thermoelelctric power, Mg-Zn Ferrites, Ceramic method, mobility of charge carries
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INTRODUCTION

In the last few years many workers investigated the electrical properties of ferrites substituted by rare earth oxides [1-5]. The electrical resistivity of ferrite has been found to increase on doping. Kolekar et al [6] studied the electrical properties of Gd substituted Cu-Cd mixed ferrite. In previous work [7, 8] we have reported the electrical study of mg-Zn ferrite substituted with Gd^{3+}. It is known that Zn^{2+} and Cd^{2+} ions have similar effect; both are diamagnetic and prefer to occupy the tetrahedral sites only [9]. Islam et al [10] has reported electrical properties of Mg-Zn ferrites. Electrical resistivity and thermo-electric power of mixed Cd-Ni-Mn ferrite have been studied by Patil et al [11]. Influence of Nd^{3+} substitution on thermoelectric power of Zn-mg ferrite has been reported by Ladgaonkar et al [12]. The effect of tetravalent ion substitution on thermoelectric power has been reported by Pujar et al [13] in Mg-Zn ferrite. The electrical properties of Mg-Cu-Zn ferrite have been studied by Eltabey et al [14]. Recently many workers [15-17] also studied the magnesium based ferrites for various applications. But the reports on rare earth substituted thermo-electric power in Mg-Zn ferrite system are rather rare.

It is interesting to investigate the behavior of conduction mechanism on substitution of Gd^{3+}in the present article in Mg-Zn mixed ferrite.   In this communication therefore the results regarding thermo-electric power of rare earth substitution on Zn-Mg ferrites are presented.

MATERIALS AND METHODS

Polycrysatlline ferrites with general formula $Zn_xMg_{1-x}Fe_{2-y}Gd_yO_4$ (x=0, 0.2, 0.4, 0.6, 0.8 and 1.0; y= 0.05 and 0.10) were prepared by standard ceramic method using AR grade oxides of Fe_2O_3, MgO, ZnO and Gd_2O_3.These pure oxides were accurately weighed accordingly to weight ratio required in the final proportions on single pan microbalance. The same were mixed together and wet milled using acetone base. Dried powder of samples was

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prisintered at 700 ^{0} C for 10 hours and sintered at 1050 ^{0} C for 24 hours, cooled and powdered. The pellets of samples were formed by applying 10^6 Kg cm^{-2} using hydrolic press. The pellets were again sintered at 1050 ^{0} C for 24 hours for better compaction. The powdered samples were characterised by XRD on philips computerised X-ray diffractometer (PW 3710) using Cukα radiation. For Tep measurent, each samle (pellet) was directly fitted against copper elelctrodes. The temperature of both surfaces of the pellet were measured with aid of chromel- Alumel thermocouple. The seebeck coefficient (α) was measured by differential method. In this method small temperature differance ΔV (20°C) was established across the sample to induce a small thermo elelctric voltage ΔT. The Seebeck Coefficient was then determined from the relation [18],

$$\alpha \ = \Delta V/\ \Delta T \tag{1}$$

The sign of the thermoelelctric vltage ΔV was taken as that of the cold surface.

RESULTS AND DISCUSSION

Characterization
From the study of X-ray diffraction pattern it was observed that all the compositions under investigation were face centered cubic spinel structure. The X-ray diffraction patterns are presented in Figure1. The calculated values of Lattice constants are presented in the Table 1. It is found that lattice constant increases with Zn^{2+} concentration. Such increase in the lattice constant due to addition of cadmium content was reported in the literature [2]. This increase in lattice constant is attributed to the difference in ionic radii of Zn^{2+} ion (0.83A^0) and Fe^{3+}ion (0.67A^0). On substitution on Gd^{3+} ion, the lattice constant found to decrease. This was also attributed to the difference in ionic radii. These results are similar as reported earlier [7, 8].

IR absorption spectra with x = 0.20 is presented in Figure 2. IR absorption spectra of all the compositions show two dominant absorption bands one around 600 cm^{-1} (v_1) and other at 400 cm^{-1} (v_2) which are characteristic of ferrite family. The absorption band observed around 600 cm^{-1} (v_1) is due to the tetrahedral or A-sites and that of around 400 cm^{-1} (v_2) is due to octahedral or B-sites respectively. These studies on characterization confirm the formation of ferrites under investigation.

Seebeck Coefficient measurement
The temperature dependence of the Seebeck Coefficient for the compositions were calculated from the relation (1) in the temperature range 300 K to 750 K and are presented in the Figures 3-4 for the samples with y = 0.05 and 0.10 respectively. From these figures, it is found that, for all samples the Seebeck Coefficient (α) is negative. This negative values of α indicates that majority charge carriers are of n- type, suggesting the conduction mechanism to be predominantly by electron hoping. Such type of behavior is also found in our previous reported values on electrical resistivity study [7]. From these it is also found that on substitution of Gd^{3+} , values of Seebeck coefficient decreases. This is due to residing of Gd^{3+} at the B-site, which decreases the Fe^{3+} ions at that site. The decrease in population of the Fe^{3+} ions at the B-site is responsible for the decrease of Seebeck coefficient. Such results have been reported for other rare earth substitution in Mg-Cd ferrite [2] and Cu-Cd ferrite[19].

The drift mobility (μ_d) of charge carriers was calculated by using the relation [20],

$$\mu_d = \frac{\exp{(\alpha/K/e)}}{2N0e\rho} \tag{2}$$

where, e= electronic charge , N_0 = the concentration of Fe^{3+} ions at the B-site, ρ =is the resistivity from dc resistivity measurement and K Boltzmann constant.

The temperature dependence of mobility obeys the relation,

$$\mu_d = \mu_0 \ \exp{(-E\mu/KT)} \tag{3}$$

Where, Eµ is the activation energy for the electron drift. The typical plot of log μ_d verses 1000/T is presented in Fig. 5. This figure indicates the increase in μ_d with increase in temperature. This may be attributed to decrease of resistivity with temperature, suggesting semiconductor behavior.

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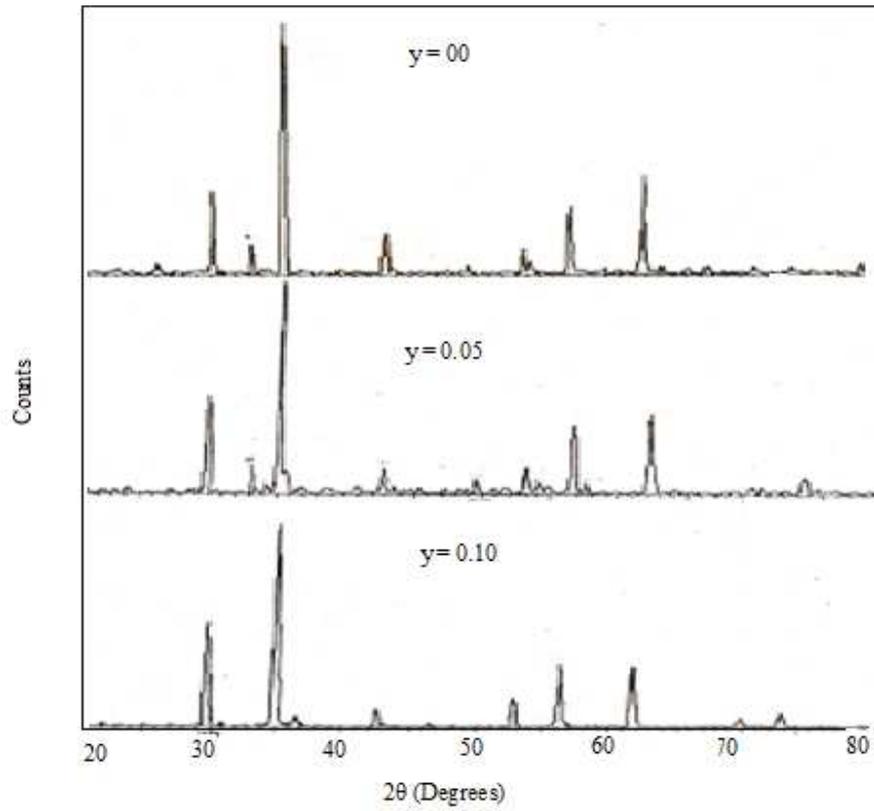
Figure 1 X-ray Diffractograms of the samples $Zn_xMg_{1-x}Fe_{2-y}Gd_yO_4$ with x= 0.4
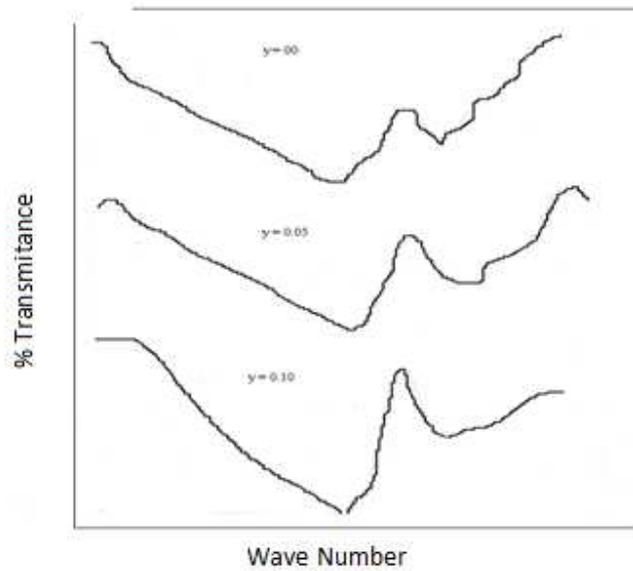
Figure 2. FTIR spectra of $Zn_xMg_{1-x}Fe_{2-y}Gd_yO_4$ with x = 0.2

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On substitution of Gd^{3+} mobility is found to decrease, which may be due to increase in the dc resistivity. The activation energy $E\mu$ obtained from log μ_d verses 1000/T plots are presented in the Table 1. From the table it can be found that the values of $E\mu$ obtained from resistivity study and from TEP study are comparable. These values decreases on substitution of Zn^{2+} and also Gd^{3+} .This suggest that the electrical conduction is mainly due to hoping mechanism on an either sites given by the relation,

$Fe^{2+} \rightarrow Fe^{3+} + e^{-1}$
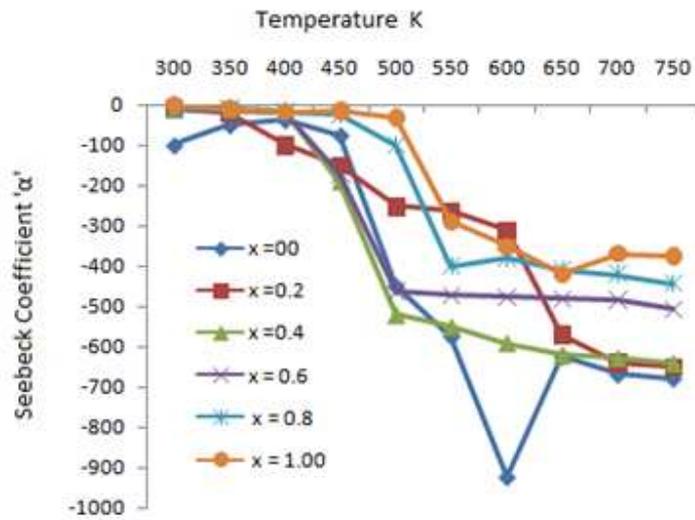
Figure 3 Variation of Seebeck coefficient with temperature $Zn_xMg_{1-x}Fe_{2-y}Gd_yO_4$ with y = 0.05
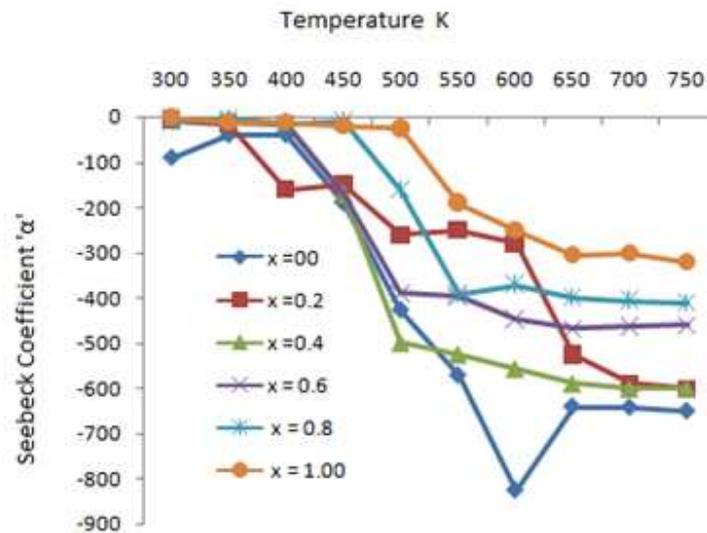
Figure 4 Variation of Seebeck coefficient with temperature $Zn_xMg_{1-x}Fe_{2-y}Gd_yO_4$ with y = 0.10

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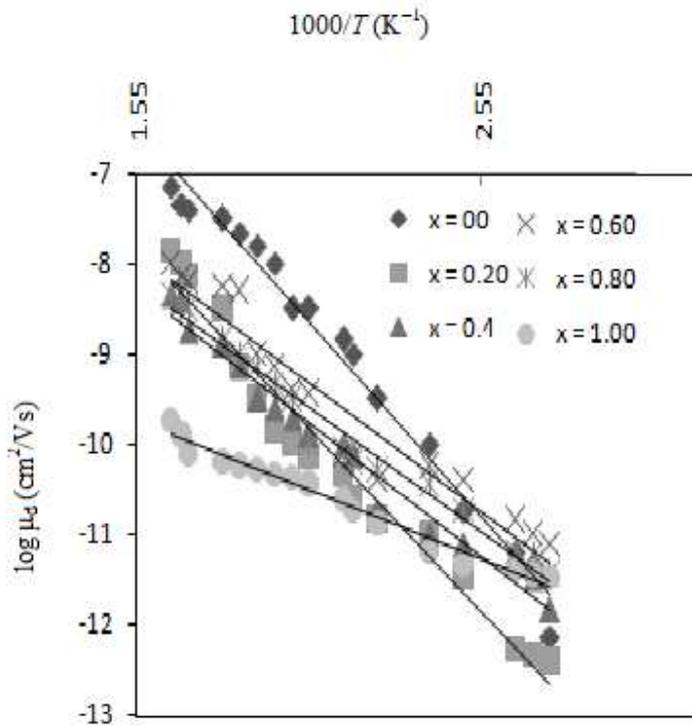
Figure 5 Graph of $\log \mu_d$ (cm²/Vs) against $1000/T$ (K⁻¹) for the composition $Zn_xMg_{1-x}Fe_{2-y}Gd_yO_4$

Table 1 Structural and electrical data of $Zn_xMg_{1-x}Fe_{2-y}Gd_yO_4$ with y= 0.05 and 0.10

Conc. Zn^{2+} (x)	Conc. Gd^{3+} (y)	Lattice constants a	Activation energy Δe (eV)		Frequency of vibration in cm⁻¹	
			Ferri region ΔEr	Para region ΔEp	ν_1	ν_2
00	0.05	8.35	0.323	0.863	571	434
0.2		8.42	0.283	0.539	575	472
0.4		8.48	0.259	0.347	587	471
0.6		8.54	0.160	0.236	563	466
0.8		8.6	----	0.207	556	451
1.0		8.66	----	0.298	540	441
00	0.1	8.34	0.365	0.865	541	434
0.2		8.4	0.248	0.596	540	431
0.4		8.46	0.354	0.278	581	470
0.6		8.52	0.086	0.248	568	465
0.8		8.58	-----	0.259	559	437
1.0		8.64	----	0.312	550	457

CONCLUSION

The study of temperature depended thermoelectric power for all the composition under investigation is found to be negative showing majority charge carriers to be n-type, indicating conduction is predominantly is electron hooping. The substituted Zn^{2+} resides at A-site and Gd^{3+} resides at B – site. These substitutions causes decrease in the values of Seebeck coefficient, which is attributed to decrease in Fe ions on both the sites. The mobility of charge carries increases with the temperature and activation energy decreases with the substitutions.

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