

Influence of Nd³⁺ substitution on thermoelectric power of Zn–Mg ferrite system

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MS received 26 August 1999; revised 17 January 2000

Abstract. Polycrystalline ferrites, $Zn_xMg_{1-x}Fe_{2-y}Nd_yO_4$ ($x = 0.00, 0.20, 0.40, 0.60, 0.80$ and 1.00 ; $y = 0.00, 0.05$ and 0.10) were prepared by standard ceramic method. X-ray diffraction study of these compositions revealed the formation of single phase spinels. Seebeck coefficient was obtained from thermo emf measurement by keeping constant temperature difference of 10 K across the pellet. The values of Seebeck coefficient were found to be negative showing majority charge carriers of n -type, suggesting the mechanism of conduction to be predominantly by electron hopping. The substitution of Nd³⁺ ion, which perhaps resides at the B-site, resulting in a decrease in the Seebeck coefficient. This decrease was assigned to the decrease of population of Fe³⁺ ion at the B-site. The activation energies calculated both from mobility plots and from dc resistivity plots were found comparable. The Fermi energy, $E_F(0)$, which was estimated by intrapolation of E_F – T curves to $T = 0$ K, was found less than the activation energy. This difference was attributed to electron hopping energy.

Keywords. Polycrystalline ferrite; rare-earth; Seebeck coefficient; electron hopping; Fermi energy.

1. Introduction

Thermoelectric properties are very useful for understanding the conduction mechanism in case of magnetic materials such as ferrites (Viswanathan and Murthy 1990). These properties depend upon method of preparation, chemical composition, substitution of foreign ions and distribution of cations among tetrahedral (A) and octahedral (B) sites (Topfer *et al* 1994). These properties of Li–Zn ferrites have been discussed by Reddy *et al* (1991), who reported the compositional dependence of the Seebeck coefficient. Murthy and Sobhanadri (1976) studied electrical conductivity and thermoelectric power, thereby dividing the ferrites into two groups, the n -type and the p -type, depending on excess and deficiency of iron, respectively. Transport properties of zinc-substituted ferrite have been reported by Ravinder and Ramana Reddy (1999), suggesting electron hopping mechanism of conduction. The effect of tetravalent ion substitution on thermoelectric power have been reported for the Mg–Zn ferrites by Pujar *et al* (1996). Influence of rare earth (La, Nd, Sm, Gd and Dy) elements substitution on thermoelectric power of zinc and magnesium containing ferrites was studied earlier (Bhosale *et al* 1997; Sattar and Elshokrofy 1997). But the reports on rare-earth substituted Zn–Mg ferrites system are rather rare. In this communication therefore the results regarding influence of Nd³⁺ substitution on Zn–Mg ferrites are presented.

2. Experimental

Polycrystalline compositions of $Zn_xMg_{1-x}Fe_{2-y}Nd_yO_4$ ($x = 0.00, 0.20, 0.40, 0.60, 0.80$ and 1.00 ; $y = 0.00, 0.05$ and 0.10) were prepared by standard ceramic method using AR grade oxides ZnO, MgO, Fe₂O₃ and Nd₂O₃. The sintering temperature was maintained at 1000°C for 24 h and then cooled slowly in the furnace at the rate of 80°C/h. To confirm the completion of solid state reaction, fine-powdered samples were subjected to X-ray diffraction using Philips make computerized X-ray diffractometer (model PW 1710), wherein CuK α radiations are employed. Seebeck coefficient was obtained from thermo emf measurements, keeping constant temperature difference of 10 K across the pelletized samples in the temperature range from 300 K to 773 K.

3. Results and discussion

X-ray diffractograms of powdered compositions reveal the formation of single phase cubic spinels, showing well-defined reflections of allowed planes, without any ambiguity. The lattice constant 'a' obeys Vegard's law, indicating thereby its increasing trend with Zn²⁺ concentration (x). This suggests the strong occupancy of Zn²⁺ ion on tetrahedral (A) site and of the substituted Nd³⁺ ion on the octahedral (B) site. These results have been reported elsewhere (Ladgaonkar *et al* 1999).

The temperature dependence of the Seebeck coefficient for the compositions were calculated from thermo emf

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measurements, $a = \Delta V/\Delta T$, in the temperature range from 300 K to 773 K and are presented in figures 1a–c for $y = 0.00, 0.05$ and 0.10 , respectively. As depicted in figure 1, the values of Seebeck coefficient, a , are found negative for higher temperature for all compositions except $x = 0.8$. For $x = 0.8$, the Seebeck coefficient reverses its sign at about 350 K and becomes negative. On Nd^{3+} substitution (figures 1b and c), the Seebeck coefficient is found negative for all temperatures. This negative value of a indicates that majority charge carriers are of n -type, suggesting the conduction mechanism to be predominantly by electron hopping. On Nd^{3+} substitution, as depicted in figures 1b and 1c, the value of Seebeck coefficient shows a decrease which perhaps could be due to Nd^{3+} ion residing at the B-site, which results in the decrease of Fe^{3+} ions at this B-site. Thus perhaps it is this decrease in the population of Fe^{3+} ions at B-site which is responsible for decrease of the Seebeck coefficient. Analogous results have been reported for rare-earth elements substitution in Mg–Cd ferrites (Bhosale *et al* 1997), and Cu–Cd ferrites (Kolekar *et al* 1995). Furthermore, from resistivity study it was found that the substitution of Nd^{3+} ion causes increase in the resistivity. Such increase in the resistivity was also reported for the rare-earth sub-

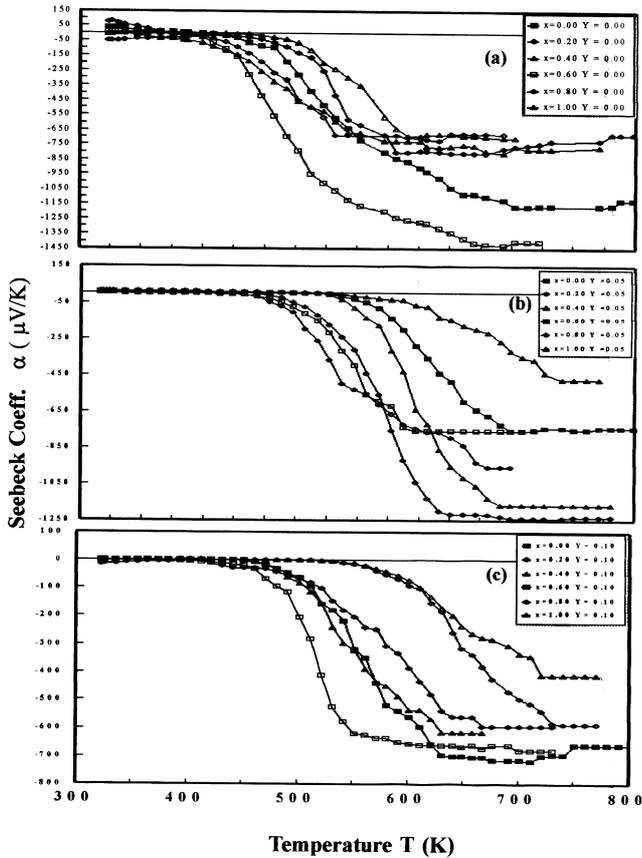


Figure 1. Graph of Seebeck coefficient, a ($\mu\text{V}/\text{K}$) against T (K) for compositions $\text{Zn}_x\text{Mg}_{1-x}\text{Fe}_{2.00}\text{Nd}_y\text{O}_4$ for (a) $y = 0.00$, (b) $y = 0.05$ and (c) $y = 0.10$.

stituted Ni–Zn ferrite by Rezlescu and Rezlescu (1997). This supports the existence of Nd^{3+} ion at the B-site, which does not participate in conduction process *per se*, but nevertheless provides hindrance to the hopping process (Kolekar *et al* 1995).

The drift mobility (m_{h}) of charge carriers was calculated using the relation (Eatah *et al* 1987),

$$m_{\text{h}} = \frac{\exp(a/k/e)}{2N_0e\mathbf{r}}, \quad (1)$$

where e is the electronic charge, N_0 the concentration of Fe^{3+} ion at the B-site, \mathbf{r} the resistivity from dc measurement, and k the Boltzmann constant. The temperature dependence of mobility obeys exponential relation i.e.

$$m_{\text{h}} = m_0 \exp(-E_m/kT),$$

where E_m is activation energy for the electron drift. The graph of $\log(m_{\text{h}})$ against $1000/T$ is plotted, and the typical graph for $y = 0.05$ is shown in figure 2. This figure indicates the increase in m_{h} with increase in the temperature. This may be attributed to decrease of resistivity with temperature suggesting semiconducting behaviour. It is found that mobility decreases with Nd^{3+} substitution, which may be due to increase of dc resistivity. The values of activation energy, E_m obtained from $\log(m_{\text{h}})$ vs $1000/T$ graphs are presented in table 1. This table also includes the acti-

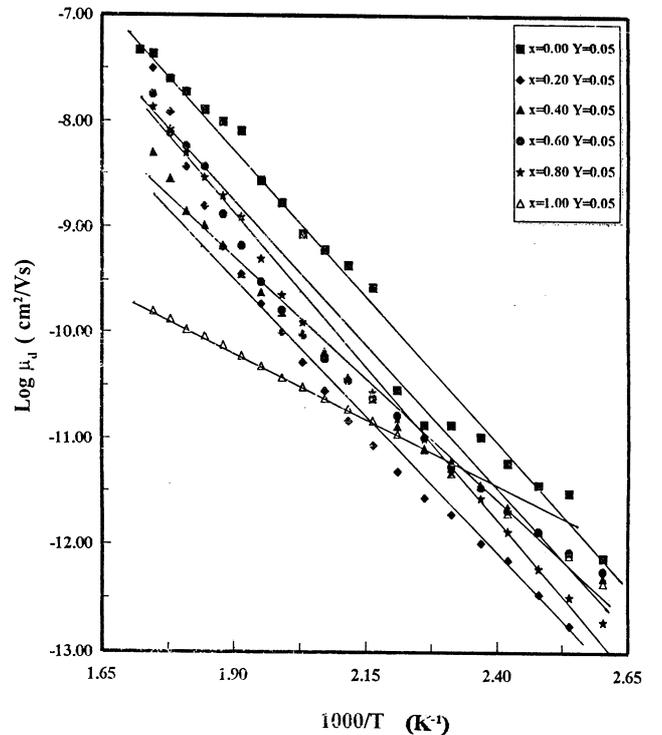


Figure 2. Graph of $\log m_{\text{h}}$ (cm^2/Vs) against $1000/T$ (K^{-1}) for the composition $\text{Zn}_x\text{Mg}_{1-x}\text{Fe}_{1.95}\text{Nd}_{0.05}\text{O}_4$.

Table 1. Experimental data for the compositions $Zn_xMg_{1-x}Fe_{2-y}Nd_yO_4$.

x	y	Activation energy from DC resistivity, ΔE (eV)		Activation energy from mobility, E_m (eV)	Fermi energy, $E_F(0)$ (eV)	
		Ferri-region	Para-region		A = 2	A = 0
0.00	0.00	0.098	0.228	0.292	0.03	0.05
0.20		0.071	0.150	0.198	0.02	0.05
0.40		0.099	0.116	0.194	0.02	0.03
0.60		0.104	0.112	0.186	0.04	0.08
0.80		–	0.108	0.183	0.02	0.05
1.00		–	0.094	0.159	0.02	0.04
0.00	0.05	0.168	0.210	0.214	0.06	0.05
0.20		0.135	0.185	0.187	0.04	0.05
0.40		0.112	0.145	0.189	0.03	0.04
0.60		0.073	0.140	0.164	0.03	0.04
0.80		–	0.118	0.124	0.02	0.02
1.00		–	0.109	0.097	0.02	0.04
0.00	0.10	0.140	0.231	0.175	0.06	0.05
0.20		0.156	0.194	0.108	0.05	0.04
0.40		0.131	0.133	0.100	0.03	0.04
0.60		0.121	0.175	0.100	0.03	0.06
0.80		–	0.143	0.108	0.02	0.04
1.00		–	0.187	0.117	0.02	0.05

vation energies obtained from dc resistivity plots, both in the ferri and para regions. The compositions for $x \geq 0.8$; $y = 0.00, 0.05$ and 0.10 show paramagnetic behaviour at and above room temperatures (Ladgaonkar *et al* 1999). From table 1 it can be found that the values of ΔE and E_m are comparable and decrease with Zn^{2+} concentration. In general, the temperature dependence of electrical conduction comes mainly from the temperature dependence of carrier mobility and type of conduction mechanism (Wang *et al* 1995). Conduction in substituted ferrites includes localization of charge carriers at lattice sites due to strong electron–phonon interaction (Eatah *et al* 1987).

In the region, where the conductivity is due to one type of charge carriers, the Fermi energy is given by (Bosman and Crevecoeur 1969),

$$E_F = e a T - A k T, \quad (2)$$

where A is dimensionless constant having values 0 and 2 depending on dominant scattering mechanism. The values of E_F were calculated and plotted as a function of temperature as shown in figure 3, for $A = 0$ and 2. E_F is found increasing with temperature suggesting n -type conductivity. The intrapolated values, $E_F(0)$, at $T = 0$ were obtained from respective plots (table 1). For n -type of conductivity, the Fermi energy, E_F , is given by (Blakemore 1962; Bosman and Crevecoeur 1969),

$$E_F = E_d + k T \log[(N_d - N_a)/N_a], \quad (3)$$

where N_d and N_a are the donor and acceptor concentrations, respectively and $N_d > N_a > 0$. Thus $E_F(0) = E_d$. On comparison the activation energy, ΔE , from resistivity graph is found to be always higher than $E_F(0)$. This difference could be attributed to the activation energy associated with hopping of electrons. Thus activation energy

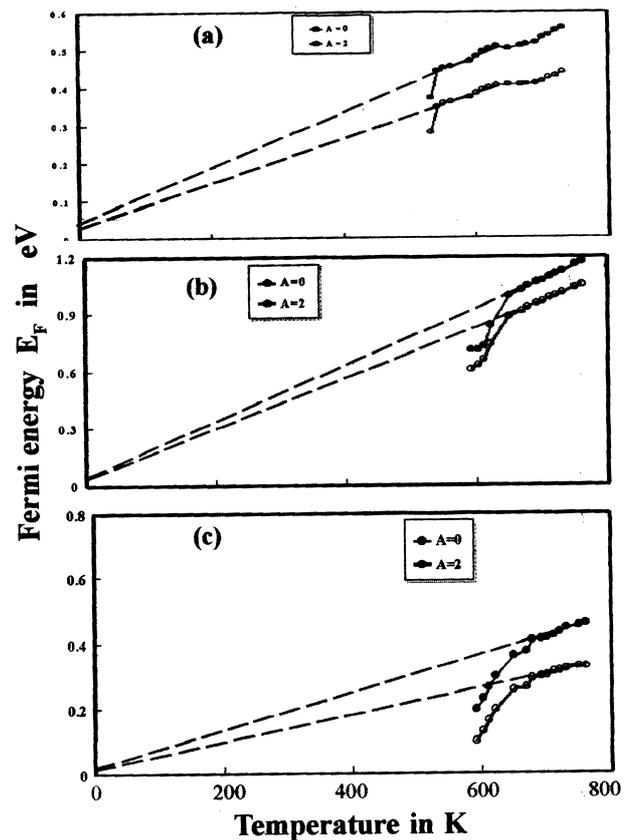


Figure 3. Graph of Fermi energy E_F (eV) against temperature T (K) for $A = 0$ and 2 for compositions $Zn_{0.20}Mg_{0.80}Fe_{2-y}Nd_yO_4$ for (a) $y = 0.00$, (b) $y = 0.05$ and (c) $y = 0.10$.

consists of two components, one that is associated with generation of electrons and the other associated with the hopping of the electrons between crystallographically equivalent site.

4. Conclusion

In this study, the Seebeck coefficient for all the compositions under investigation is found to be negative showing majority charge carriers to be of *n*-type, suggesting thereby that the mechanism of conduction is predominantly by electron hopping. The substituted Nd³⁺ ions reside at the B-sites and causes decrease in the value of the Seebeck coefficient which is perhaps attributable to the decrease in the population of Fe³⁺ ions at the B-site. Furthermore, the activation energies from dc resistivity and mobility are found comparable, while Fermi energy shows an increasing trend with temperature, supporting *n*-type of conductivity.

Acknowledgement

One of the authors (BPL) is thankful to the University Grants Commission, New Delhi, for the award of a teacher fellowship under faculty improvement programme.

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