Conduction in Mn substituted Ni–Zn ferrites

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Abstract. The d.c. electrical resistivity ' ρ ' and thermoelectric power ' α ' are studied as a function of temperature for Mn substituted ferrites with general formula $\text{Zn}_{0.3}\text{Ni}_{0.7+x}\text{Mn}_x\text{Fe}_{2-2x}\text{O}_4$. At lower Mn concentrations, the increase in d.c. resistivity is attributed to the hindering of Verwey mechanism $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ due to stable bonds of $\text{Mn}^{3+} + \text{Fe}^{2+}$ pair. The decrease in resistivity at higher Mn concentrations (i.e. when $x > 0.15$) is attributed to the formation of Mn^{3+} cluster and $\text{Ni}^{2+} \rightleftharpoons \text{Ni}^{3+}$. The activation energy values show one to one correspondence with resistivity values. The compositional variation of thermoelectric power shows n -type behaviour for the samples with $x < 0.2$ whereas p -type behaviour for the samples with $x \geq 0.2$. The $p-n$ transition is attributed to the formation of Ni^{3+} , Fe^{2+} + vacancies which act as p -type carriers. The temperature dependences of α , ρ , and mobility clearly confirm the conduction mechanism to be due to polaron hopping.

Keywords. Ferrite; resistivity; thermoelectric power; polaron hopping.

1. Introduction

The diversity in properties of ferrites have paved the way for the development of wide variety of ferrites for applications in microwave devices, permanent magnets and electrical and electronic components. Substituted nickel ferrites have been the subject of extensive investigations because of their microwave applications (Slick 1980; Khan and Misra 1985; Srivastav and Patni 1989). Specially Ni–Zn ferrites are used in high frequency and pulse field applications. The electrical and magnetic properties of Ni–Zn ferrites have been studied by many workers (Ishino and Naramiya 1987; Bhise *et al* 1991). It is observed that incorporation of diamagnetic, tetravalent and pentavalent ions in these ferrites sufficiently improves their electrical properties whereas these ions reduce magnetization and permeability values. In the present paper we report the electrical properties of Mn substituted Ni–Zn ferrites.

2. Experimental

The ferrites with chemical formula $\text{Zn}_{0.3}\text{Ni}_{0.7+x}\text{Mn}_x\text{Fe}_{2-2x}\text{O}_4$ where x varied from 0.0 to 0.4 were prepared by ceramic method. AR grade oxides NiO, MnO_2 , ZnO and Fe_2O_3 were mixed in required proportions in an agate mortar in acetone medium. The samples were then presintered at 700°C for 10 h in air medium and slowly cooled to room temperature. The presintered powder was milled and sieved to obtain a fine powder. Pellets were prepared by subjecting a small quantity of powder to a pressure of about 12×10^6 kg/mt² for 5 min by keeping it in a die of diameter 1.5 cm and these were finally sintered at 1000°C for about 24 h in air, cooling to room temperature was carried out at the rate of 80°C/h. X-ray diffractograms were obtained by using CuK_α radiation to confirm the completion of solid state reaction. The d.c. resistivity

Table 1. Compositional variation of resistivity, Seebeck coefficient and activation energy from resistivity and mobility for the system $\text{Zn}_{0.3}\text{Ni}_{0.7+x}\text{Mn}_x\text{Fe}_{2-2x}\text{O}_4$.

Mn content (x)	d.c. resistivity at 100°C, ρ , (K Ω m)	Seebeck coefficient at 300 K α (μ V/K)	Activation energy from resistivity		Activation energy from mobility (eV)
			Ferri-region (eV)	Para-region (eV)	
0.05	63.68	-195	0.52	0.37	0.52
0.10	187.10	-082	0.61	0.41	0.74
0.15	561.39	-50	0.84	0.50	0.55
0.20	53.55	+30	0.58	0.62	0.56
0.30	23.40	+10	0.49	0.54	0.58
0.40	4.13	+25	0.45	0.55	0.66

Figure 1. Variation of $\log \rho$ with $1/T$ for $x = 0.0, 0.05, 0.10, 0.15$.

with temperature in the range 300–800 K was measured by a two-probe method. The Seebeck coefficient was measured at various temperatures from room temperature to Curie temperature by keeping a temperature difference of 20 K across the pellet. For better ohmic contacts, silver paste was applied on both the surfaces of the pellet.

3. Results and discussion

Compositional variation of resistivity and Seebeck coefficient are noted in table 1. This shows that the resistivity increases with Mn up to $x = 0.15$ and then decreases. The variation of $\log \rho$ with $1/T$ given in figure 1 shows linear behaviour in nature and the activation energies calculated from these plots for ferri-region and para-region are given in table 1. The plots of Seebeck coefficient with temperature are given in figure 2. For the samples with $x = 0.05, 0.1$ and 0.15 , α values are negative and they remain

Figure 2. Temperature variation of Seebeck coefficient for the system $\text{Zn}_{0.3}\text{Ni}_{0.7+x}\text{Mn}_x\text{Fe}_{2-2x}\text{O}_4$.

negative throughout the temperature range. For $x = 0.2$ and 0.3 , α values change from +ve to -ve whereas the sample $x = 0.4$ shows only +ve values for α throughout the temperature range. The samples with $x = 0.2$ and $x = 0.3$ show p to n type transition at about 325 K and 550 K respectively. For the samples with $x < 0.2$, $|\alpha|$ values increase with temperature up to about 500 K and then decrease. The cusp like minima increasingly becomes broader and then disappears for $x = 0.2$. The remaining samples show that $|\alpha|$ is nearly independent of temperature.

It has been pointed out in our earlier studies that oxido reduction process appears during sintering in air atmosphere.

Here (O) represents a cation vacancy (Tailhades *et al* 1992).

Simsa (1966) proposed that the pair $\text{Fe}^{2+} + \text{Mn}^{3+}$ at an octahedral site is more stable and has lower energy than the Fe^{2+} ion. In the present system 2 Fe^{3+} ions are replaced by Mn^{4+} and Ni^{2+} . Therefore with increasing Mn contents, more number of Fe^{2+} and Mn^{3+} bonds are formed and hence there is an increase in the resistivity. The decrease in resistivity can be explained on the basis of clusters of Mn^{3+} ions (Goodenough 1965). These clusters effectively reduce the concentration of stable bonds of $\text{Fe}^{2+} + \text{Mn}^{3+}$ and conduction may be due to more number of Mn ions at octahedral sites. It is interesting to note that activation energy in ferriregion follows the trend of ρ with composition.

The compositional variation of n to p type conductivity can be related to the presence of Fe^{2+} and Ni^{3+} ions respectively. The predominant conduction in Ni–Zn ferrites is due to the presence of Ni ions in the octahedral sites, favouring the conduction mechanism such as $\text{Ni}^{2+} + \text{Fe}^{3+} \rightleftharpoons \text{Ni}^{3+} + \text{Fe}^{2+}$. In $\text{Ni}_x\text{Fe}_{3-x}\text{O}_4$ system it is stated that as x becomes larger than one, the Ni^{2+} ions become Ni^{3+} ions in order to maintain charge neutrality and continue to stay at octahedral site (Wilson and Douglass 1981). Also NiO has an affinity for oxidation resulting in the formation of Ni^{3+} ions. Therefore in the present system Ni ions are increased which can favour the formation of Ni^{3+} ions. Again, cation vacancies, if present, form cation $\text{Fe}^{3+} + \text{vacancy}$ complex which act as p -type carrier (Khan and Misra 1985). Hence, n to p transition takes place as x varies in the present system. Here, it is also noted that Mn is a John–Teller ion and it has $3d^4$ configuration. It seems likely that the large tetragonal distortions associated with John–Teller ions are effective in anchoring oxygen vacancies. Therefore, the conduction due to Mn, such as $\text{Mn}^{4+} \rightleftharpoons \text{Mn}^{3+}$, favours the conduction process in these materials.

The different regions with changing slopes have been observed in resistivity versus $1/T$ plots for many ferrites (Bhise *et al* 1992; Patil *et al* 1993). This is attributed to the change in the conductivity mechanism. The activation energies calculated by us in ferri-region are greater than 0.5 eV which are much larger than the ionization energy 0.1 eV of donors or acceptors. It is also much larger than electron-transition energy of 0.2 eV such as $\text{Fe}^{2+} \rightleftharpoons \text{Fe}^{3+}$ and 0.3 eV energy of $\text{Mn}^{3+} \rightleftharpoons \text{Mn}^{4+}$. Hence the possibility of band type of conduction is ruled out. The mobility values are calculated by using α and ρ values at different temperatures (Ghani 1983). The activation energies calculated from mobility agree with those activation energies calculated from conductivity in ferri-region. This in itself suggests that the conduction phenomenon in present system is due to polaron-hopping.

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