

Study on Conduction Mechanism, Ferrous Ion Concentration, Oxygen Deficiency, and Fermi Energy Determination from a Thermal Variation of Seebeck Coefficient Measurement for $Zn_{0.3}Mn_{0.7+x}Si_xFe_{2-2x}O_4$ Ferrite Series

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Abstract The compositional and temperature ($T = 300 - 525$ K) dependence of Seebeck coefficient measurement has been carried out on microcrystalline ferrite samples of $Zn_{0.3}Mn_{0.7+x}Si_xFe_{2-2x}O_4$ ($x = 0.0, 0.1, 0.2$ and 0.3) series. The probable conduction mechanism is the exchange of electrons between Fe^{3+} and Fe^{2+} ions on the octahedral interstitial site of the spinel structure. The absolute concentration of ferrous and ferric ions has been deduced that used to determine the actual occupancy of metallic cations, oxygen deficiency, and to describe the compositional variation of dc resistivity. Finally, the Fermi energy values at $T = 0$ K have been derived.

Keywords Ferrites, Thermoelectric power study, Conduction mechanism, Fermi energy

1. Introduction

The Seebeck coefficient is also referred to as thermoelectric sensitivity, thermopower, and thermoelectric power. The Hall coefficient and Seebeck coefficient measurements are the most promising characterization techniques to understand responsible mechanisms for electrical conduction in various classes of materials. Regarding low mobility and high resistivity materials, for instance, ferrites, and perovskites, the Hall voltage measurement becomes difficult. The only alternative in such a case is the temperature dependence of Seebeck coefficient measurement. The thermoelectric power measurement is very simple and carrier type (holes or electrons) accountable for the conduction process can be decided without any ambiguity. This is further used to determine many important parameters, charge carrier density, Fermi energy, mobility of charge carrier, oxygen deficiency, activation energy, charge disproportionation, etc., [1-5].

Restricted to thermopower study on spinel structured ferrite series, in recent years (2016 - 2020), very limited research communications are available in literature. Polycrystalline sample of magnesium ferrite ($MgFe_2O_4$) synthesized by spark plasma and solid-state reaction sintering processes [6], non-stoichiometric ferrite system, $Mg_{0.5+x}Cu_xZn_{0.5}Fe_{1.9}O_{4-\delta}$ ($x = 0.0 - 0.3$) [7], Ni^{2+} - substituted Mg-Cu-Zn ferrites [8], tetravalent Sn^{4+} substituted copper ferrite [9] and $Li_{0.5-0.5x}Cu_xFe_{2.5-0.5x}O_4$ ($x = 0.0 - 1.0$) series [1] have been investigated for their thermoelectric sensitivity. The thermoelectric properties of composites of carbon nanotubes, multiwalled carbon nanotubes, graphene and $Mn_{0.7}Zn_{0.3}Fe_2O_4$ spinel ferrite synthesized by spark plasma sintering process have been studied by Zhang et al. [10-12]. Thermopower study has been carried out on nanoparticles of $Mn_xZn_{1-x}Fe_2O_4$ ($x = 0.0 - 1.0$) [13], $NiSm_xFe_{2-x}O_4$ [14], $Co_xMn_{0.5-x}Zn_{0.5}Fe_2O_4$ ($x = 0.0, 0.1, 0.3$ and 0.5) [15], and $Li_{0.15}Ni_{0.5}Sm_{0.1}Fe_{2.15}O_4$ [16] spinel ferrite systems prepared by co-precipitation technique/citrate-gel auto combustion route.

In recent years, the structural, microstructural, bulk magnetic, electric and dielectric characteristics of ferrite series, $Zn_{0.3}Mn_{0.7+x}Si_xFe_{2-2x}O_4$ with $x = 0.0, 0.1, 0.2$ and 0.3 , by means of energy dispersive analysis of X-rays (EDAX),

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X-ray powder diffractometry (XRD), scanning electron microscopy (SEM), bulk magnetization ($H_{max} = 2.5$ kOe, $T = 80$ K and 300 K), temperature dependence of low field (0.5 Oe) ac (263 Hz) susceptibility measurement ($T = 300$ K – 525 K), temperature dependence of dc resistivity measurement ($T = 300$ K – 773 K), current versus voltage ($I - V$) characteristics ($T = 300$ K – 673 K and $V = 0 - 400$ V), frequency ($f = 20$ Hz – 1 MHz) and temperature ($T = 300$ K – 673 K) dependent permeability and dielectric constants measurements have been investigated [17-23].

In this communication, the thermal variation of Seebeck coefficient (α) measurement carried out on this well-characterized system, $Zn_{0.3}Mn_{0.7+x}Si_xFe_{2-2x}O_4$ ($x = 0.0 - 0.3$), has been reported. The values of α have been used to calculate ferrous ion concentration, oxygen deficiency, and Fermi energy.

2. Experimental Details

The technical particulars related to the preparation of four single-phase, microcrystalline compositions of ferrite series, $Zn_{0.3}Mn_{0.7+x}Si_xFe_{2-2x}O_4$ where $x = 0.0, 0.1, 0.2$ and 0.3 , by high-temperature solid-state reaction method, phase analysis, and structural parameters including cation distribution determination from X-ray diffraction line intensity calculations [20,22] and thermoelectric power measurement are well described in [2-5].

3. Results and Discussion

The values of the thermoelectric power coefficient (α) have been calculated by $\alpha = \Delta V / \Delta T$, where ΔV is the electric potential difference generated as a result of temperature difference (ΔT) between the hot junction temperature (T) and the cold junction temperature (T_c). The α values show small variation ($\pm 1.0\%$) during the heating and cooling cycles of measurement. In Fig. 1, the $\alpha(T)$ plots for the system, $Zn_{0.3}Mn_{0.7+x}Si_xFe_{2-2x}O_4$ ($x = 0.0, 0.1, 0.2$ and 0.3) are depicted. It is found that for all the compositions α is negative throughout the temperature range studied. This suggests that electrons are the majority charge carriers or dominant conduction mechanism is n-type in the series. Earlier, Ivanovskaya *et al.* [24] have shown that Mn-Zn ferrite materials synthesized without controlled parameters (high-pressure preparation of material in an oxygen atmosphere) possess oxygen vacancies, that turns out to be a partial reduction of ferric ion (Fe^{3+}) into ferrous ion (Fe^{2+}) in the system. The existence of Fe^{3+} ions in other valance states (Fe^{2+} or Fe^{4+}) results in interesting changes in the electrical characteristics of ferrites [24-26]. At the octahedral (B-) sites of the spinel structure, the exchange of electron takes place between Fe^{3+} and Fe^{2+} by the conduction mechanism: $Fe^{2+} \leftrightarrow Fe^{3+} + e^-$.

When in any system, two types of hopping conduction mechanisms are assumed to be involved, the parameters, the

concentration of substituted metallic cation (x), and measurement temperature will decide the dominance of one mechanism over the other mechanism. If the hole exchange mechanism given by $Mn^{3+} \leftrightarrow Mn^{2+} + e^-$ (p-type conduction) is dominating over the electron exchange mechanism that takes place by $Fe^{2+} \leftrightarrow Fe^{3+} + e^-$ in the system under investigation, $Zn_{0.3}Mn_{0.7+x}Si_xFe_{2-2x}O_4$, the ferrite composition might conduct as a p-type semiconducting material or vice versa.

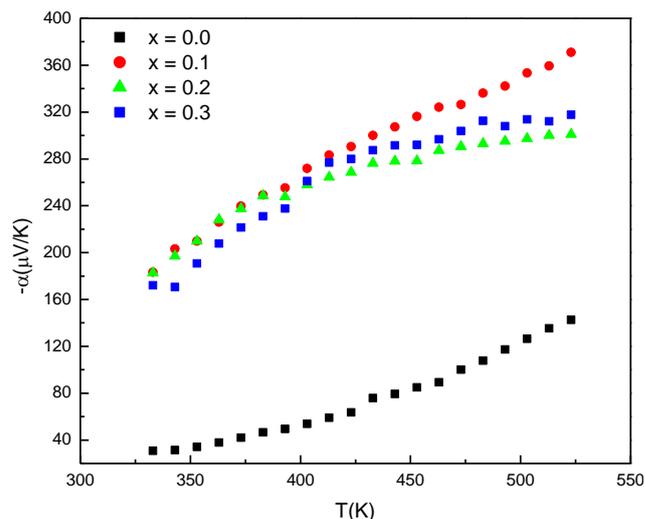


Figure 1. Seebeck coefficient (α) against hot junction temperature plots for $Zn_{0.3}Mn_{0.7+x}Si_xFe_{2-2x}O_4$ series

A careful examination of Fig. 1 shows that the Seebeck coefficient (α) initially increases rapidly with temperature from $T = 300 - 425$ K while α increases slowly with a further increase in temperature ($T \geq 425$ K) for all the compositions. This observed variation in $\alpha(T)$ curves can be explained as follows. In n-type semiconducting material, owing to the loss of electrons, the hot surface becomes positively charged due to the diffusion of these liberated electrons. The hopping mechanism, $Fe^{2+} \leftrightarrow Fe^{3+} + e^-$, turns out to be most probable on increasing temperature that produces electrons. The accumulation of such electrons at the cold surface results in the development of potential difference (ΔV), thus α increases rapidly during $T = 300 - 425$ K. The observed small variation in α with T for $T \geq 425$ K is mainly due to the saturation in the generation of electrons and electrons-holes recombination in the system. When valence electrons are given energy equal or greater than the energy band gap, they will be transferred to the conduction band and recombination of an electron-hole occurs. Following the classifications proposed by Bashikiriv *et al.* [27], the significant variation in α with T (Fig. 1) suggests that the ferrite materials under investigation are non-degenerate semiconductors.

The thermoelectric power (α) in the instance of hopping conduction is given by the formula as suggested by Heikes formula [28]:

$$\alpha = -\frac{k}{e} \left[\frac{S_T}{k} + \ln \frac{1-c}{c} \right] \quad (1)$$

where k and e are Boltzmann's constant and electronic charge, respectively, S_T is the temperature-independent effective entropy transport by the charge carriers. According to Goodenough et al. [29], the S_T/k is commonly insignificant for oxide/ferrite systems. It contributes not more than 10 $\mu\text{V/K}$ and thus neglected in the above expression (1). The ratio of the number of carriers in the states (n) to the number of available states (N), i.e., n/N is denoted by ' c '. Thus, the above eq. (1) can be rewritten as:

$$\alpha = -\frac{k}{e} \left[\ln \frac{1-c}{c} \right] \quad (2)$$

A more generalized formula for the oxide systems in which cation in two different valence states, $M^{n+}/M^{(n+1)+}$, is present has been derived by Doumerc et al. [30] and accordingly:

$$\alpha = -\frac{k}{e} \ln \frac{1-c}{c} = \frac{k}{e} \ln \frac{1-c_h}{c_h} \quad (3)$$

Here, number of holes (p) per active transport site (N) i.e., the hole concentration (c_h) is given by $c_h = 1-c = p/N$. Based

on the assumption that ' N ' is equal to the total number of ferrous and ferric ions residing at the octahedral environment and ' n ' is the number of ferric ions at the B-site, above eq. (3) becomes:

$$\alpha = -\frac{k}{e} \ln \left[\frac{\text{Fe}_B^{2+}}{\text{Fe}_B^{3+}} \right]$$

$$\left[\frac{\text{Fe}_B^{2+}}{\text{Fe}_B^{3+}} \right] = \exp \left(-\frac{\alpha \cdot e}{k} \right) \quad (4)$$

For various types of oxides systems such as spinel ferrites [5,31], magnetite [32], hausmannite [33], and manganite perovskites [3], this has been found suitable for the determination of the relative concentration of ferrous ion to ferric ion on the B-site.

The Seebeck coefficient values registered at $T = 373$ K have been used to determine the relative concentration of $\text{Fe}^{2+}/\text{Fe}^{3+}$, the absolute ferrous ion concentration, and the product of (Fe^{2+}) (Fe^{3+}) ions residing at the octahedral interstitial sites, and the same have been summarized in Table 1. Based on this the actual distribution of cations and oxygen deficiency (δ) for each composition has been determined and shown in Table 2.

Table 1. Seebeck coefficient (α), the cationic concentration at $T = 373$ K and Fermi energy at $T = 0$ K for $\text{Zn}_{0.3}\text{Mn}_{0.7+x}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$ series

Mn-Si content (x)	α ($\mu\text{V/K}$) (373K)	$\frac{(\text{Fe}_B^{2+})}{(\text{Fe}_B^{3+})} 10^{-2}$	(Fe_B^{2+}) (wt%)	$(\text{Fe}_B^{2+})(\text{Fe}_B^{3+})^* 10^{-1}$	$E_F(0)$ (0K) (eV)
0.0	-041.9	61.52	28.35	6.43	0.170
0.1	-239.6	06.22	02.74	1.34	0.174
0.2	-237.3	06.38	02.58	1.22	0.156
0.3	-221.3	07.68	02.88	1.24	0.168

Table 2. Occupancy of cations and oxygen deficiency (δ) for spinel structured ferrite series $\text{Zn}_{0.3}\text{Mn}_{0.7+x}\text{Si}_x\text{Fe}_{2-2x}\text{O}_4$

Mn-Si content (x)	Actual cation distribution	(δ)
0.0	$(\text{Zn}^{+2}_{0.25}\text{Mn}^{+2}_{0.40}\text{Fe}^{+3}_{0.35})[\text{Zn}^{+2}_{0.05}\text{Mn}^{+2}_{0.30}\text{Fe}^{+3}_{1.02}\text{Fe}^{+2}_{0.63}]\text{O}_{3.68}$	0.32
0.1	$(\text{Zn}^{+2}_{0.25}\text{Si}^{+4}_{0.10}\text{Mn}^{+2}_{0.43}\text{Fe}^{+3}_{0.22})[\text{Zn}^{+2}_{0.05}\text{Mn}^{+2}_{0.37}\text{Fe}^{+3}_{1.49}\text{Fe}^{+2}_{0.09}]\text{O}_{3.95}$	0.05
0.2	$(\text{Zn}^{+2}_{0.25}\text{Si}^{+4}_{0.15}\text{Mn}^{+2}_{0.45}\text{Fe}^{+3}_{0.15})[\text{Zn}^{+2}_{0.05}\text{Si}^{+4}_{0.05}\text{Mn}^{+2}_{0.45}\text{Fe}^{+3}_{1.36}\text{Fe}^{+2}_{0.09}]\text{O}_{3.95}$	0.05
0.3	$(\text{Zn}^{+2}_{0.25}\text{Si}^{+4}_{0.21}\text{Mn}^{+2}_{0.48}\text{Fe}^{+3}_{0.06})[\text{Zn}^{+2}_{0.05}\text{Si}^{+4}_{0.09}\text{Mn}^{+2}_{0.52}\text{Fe}^{+3}_{1.24}\text{Fe}^{+2}_{0.10}]\text{O}_{3.95}$	0.05

It is found that the percentage variation of the Fe^{2+} -ion concentration and the product of (Fe^{2+})(Fe^{3+}) ions on the octahedral sites is $\sim 91\%$ for a given range of compositions (Table 1). This suggests that the percentage variation in dc resistivity (ρ_{dc}) value cannot exceed 91% if these two parameters are responsible for the observed change in ρ_{dc} . Recently, it has been found that the percentage variation in ρ_{dc} as a function of composition (x) at $T = 373$ K is $\sim 90\%$ [20].

In solids, the energy of the highest filled state in the electronic band structure at $T = 0$ K is referred to as the

Fermi energy, $E_F(0)$. An effort has been made to determine $E_F(0)$ by extrapolating values of $E_F(T)$ to $T = 0$ K. The region in which electric conduction solely owing to either of the charge carriers (electrons or holes, not both), the α and E_F are correlated by the relation [34]:

$$E_F(T) = e\alpha T - AkT \quad (5)$$

where ' A ' is a dimensionless constant related to the kinetic energy of the charge carrier. The temperature dependence of E_F for $A = 0$ and $A = 2$ are shown in Fig. 2 for all the compositions.

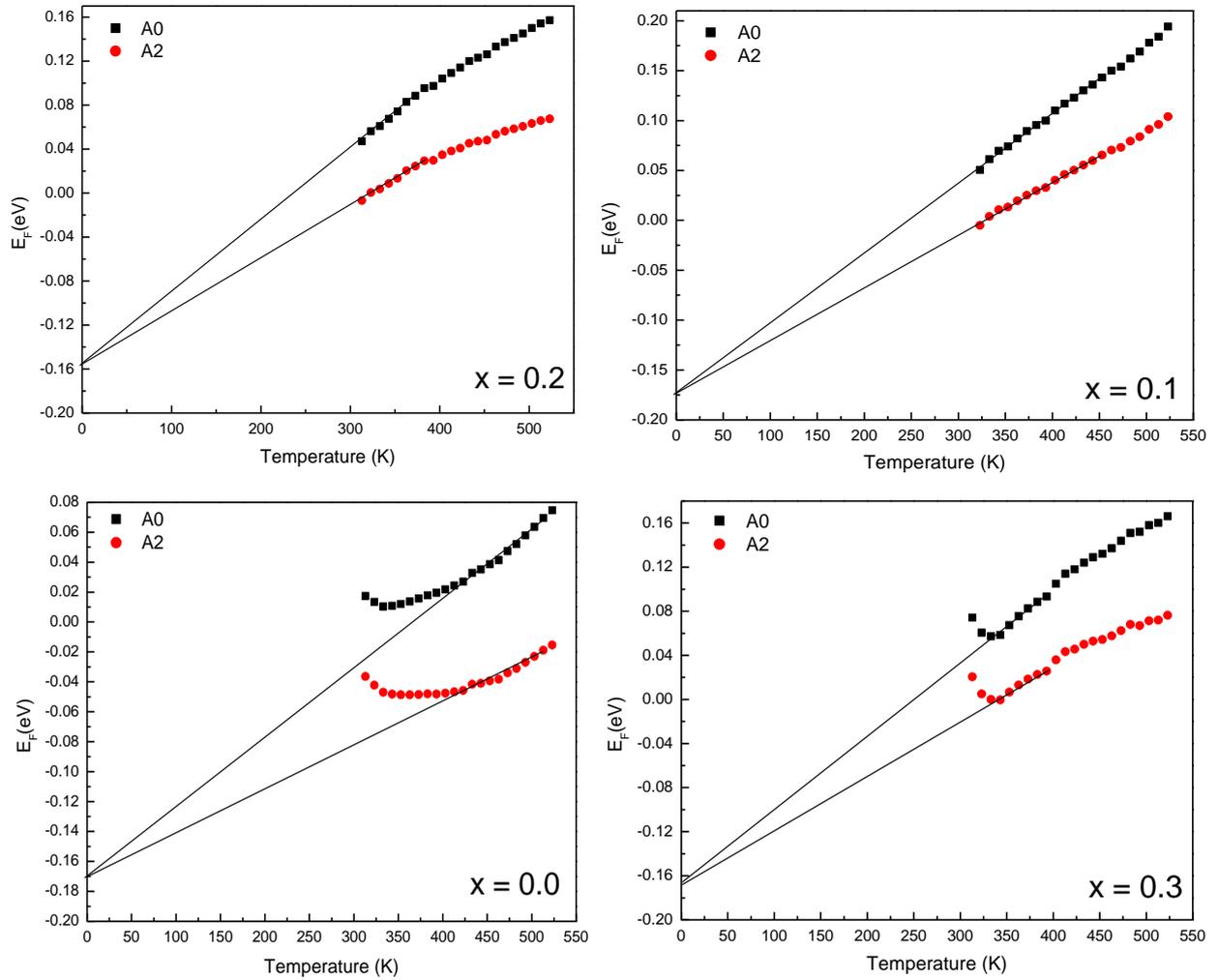


Figure 2. Thermal variation of Fermi energy for $Zn_{0.3}Mn_{0.7+x}Si_xFe_{2-2x}O_4$ series

The extrapolation of these two curves of E_F intercepts the y-axis at a specific point ($T = 0$ K), yield $E_F(0)$. The magnitude $E_F(0)$ has been taken into consideration as $E_F(0)$ cannot be negative [35]. The $E_F(0)$ shows small variation with Mn-Si concentration (x) in the series $Zn_{0.3}Mn_{0.7+x}Si_xFe_{2-2x}O_4$ (Table 1). The observed difference between the activation energy values ($E = 0.21$ eV to 0.27 eV for $x = 0.0$ to 0.3 compositions) determined from $\log_{10} p_{dc}$ against reciprocal of temperature plots [20] and $E_F(0)$ ($E > E_F(0)$) may be ascribed to the activation energy analogous to hopping of charge carriers. Consequently, total activation energy is made up of two terms, kinetic energy related to the generation of charge carriers and kinetic energy associated with the hopping of charge carriers between crystallographically equivalent sites.

4. Conclusions

The following intriguing conclusions are drawn based on the compositional and thermal variation of thermoelectric power study on ferrite series, $Zn_{0.3}Mn_{0.7+x}Si_xFe_{2-2x}O_4$ ($x = 0.0 - 0.3$).

The ferrites under investigation are non-degenerate semiconducting materials and the exchange of electrons among ferrous (Fe^{2+}) and ferric (Fe^{3+}) ions on the octahedral site is the governing mechanism of electrical conduction. The relative and absolute concentration of ferrous and ferric ions, as well as oxygen deficiency, can be determined from the temperature-dependent thermopower measurement. The Fermi energy shows compositional variation consistent with the variation of Fe^{2+} - ions in the system.

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