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Thermoelectric Studies of MgCuZn Ferrites

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Abstract: A series of MgCuZn ferrites with generic formula $Mg_{0.5-x}Cu_xZn_{0.5}Fe_2O_4$ where x = 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 are synthesized by conventional double sintering technique. X-ray diffraction studies have revealed single phase spinal structure. The series of samples are investigated for thermo emf in the temperature range of 40°C to 400°C at an interval of 5°C with 10°C temperature gradient across the sample. From these measurements Seebeck coefficient α and corresponding Fermi energies are calculated for all the samples throughout the investigated temperature region. The compositional variation of Seebeck coefficient at room temperature showed a maximum at x = 0.1 copper concentration. All the samples studied have attained a maximum Seebeck coefficient at certain temperature. All the samples studied have exhibited negative Seebeck coefficient in the entire temperature region of investigation suggesting that these MgCuZn ferrites come under n– type semiconductors.
Keywords: Ferrites, X-ray diffraction, Thermoelectric power, Seebeck coefficient, Fermi energy.

Introduction:

While electrical conduction is a vital property in itself type of conducting carrier also plays a crucial role in designing the material for the required application. In the case of low–mobility semiconductors such as ferrites, study of thermoelectric power is the only alternative. Studies on thermoelectric power help in identifying the type of carrier apart from understanding the conduction mechanism in ferrites. These properties depend on many factors such as chemical composition, method of preparation, cation distribution in tetrahedral (A-) and octahedral (B-) sites, sintering temperatures etc[1]. Furthermore a thermoelectric power study of ferrites – oxide materials is important firstly due to the conversion of thermal energy to electrical energy. Secondly oxides are comparatively stable, abundant in nature, reliable and renewable energy sources than tellurides such as PbTe- and GeTe [2].

MgCuZn ferrites are competent as core materials for high frequency applications due to their equally good electrical and magnetic properties as those of NiZn and NiCuZn ferrites with an added advantage of cost effectiveness and environmental friendly [3]. Many reported the thermoelectric power on Mg based ferrite systems such as ZnMgNd, NiMgCuZn, NiMgZnCo, MgZn, MgTi and Mg-Fe-O [3–8]. Thermoelectric property of this particular MgCuZn ferrite system is not yet reported. In view to understand the type of carriers, conduction mechanism in these MgCuZn ferrites the composition and temperature dependence of thermoelectric power is studied in the present work.

Experimental Technique:

$Mg_{0.5-x}Cu_xZn_{0.5}Fe_2O_4$ where x = 0.05, 0.1, 0.15, 0.2, 0.25 and 0.3 ferrite samples are synthesized from analytical grade MgO, ZnO, CuO and Fe_2O_3 by conventional double sintering method. All the samples are finally sintered temperature of 1250°C in Zn atmosphere. Pellets of diameter 1cm and thickness of 0.2cm are first characterized by X-Ray diffraction studies (PM 1730, Germany using Cu Kα radiation) for phase confirmations.

The surfaces of the sample pellet are coated with silver paste (Du Pont) for good ohmic contacts. The pellet is placed in the sample holder and then the entire cell is kept into a tubular furnace for the measurement of thermoelectric power. A temperature difference of 10°C across the pellet is maintained using a small independent micro-furnace fitted with the sample holder assembly. The thermo–emf across the pellet is measured with a dc micro voltmeter (Philips). The thermo–emf measurements were made after the attainment of thermal equilibrium. The temperatures have been measured using calibrated chromel–alumel thermocouple. The measurements were made in the temperature range of 40 to 400°C at intervals of 5°C. Seebeck voltage V_s is determined by using the relation $V_s = \alpha(T_2-T_1)$ where the constant of proportionality (α) is known as the thermoelectric power and has the dimensions of volt per degree. It is also referred to as Seebeck coefficient.

Results and Discussion:

The typical X-ray diffraction (XRD) patterns of the investigated ferrite series with x = 0.10 and 0.25 shown in Fig. 1, exhibit single phase spinel structure of the ferrite samples is observed. The density of all the samples measured from Archimedes principle is given in Table 1. As the copper concentration increased the densities of the present ferrite series increased with a slope change at x= 0.1 concentration. The increase in density may be due to increased compactness in the ferrites during liquid phase sintering. Copper oxide at elevated temperature gets decomposed to Cu_2O which has low melting point [9]. It is expected that at temperatures even less than the melting point of Cu_2O a eutectic copper rich region facilitate liquid phase sintering of the ferrite. A similar behaviour was reported in previous study [10] in iron deficient MgCuZn ferrite series sintered in conventional and microwave furnaces. The concentration x = 0.1 seems to be critical concentration of copper at which an abrupt change in the properties of MgCuZn ferrites are already reported [11,12]. The slope change in density and the peak value of thermoelectric power studies (values in Table 1) at x = 0.1 once again confirms the critical limit of copper concentration in MgCuZn ferrites. At low concentrations of copper it appears that there is an abrupt change in the population of Fe^{3+} and Cu^{2+} ions. And hence the Seebeck coefficient showed a large negative value. At this composition Rezlescu et al [13] also have reported high resistivity behaviour.

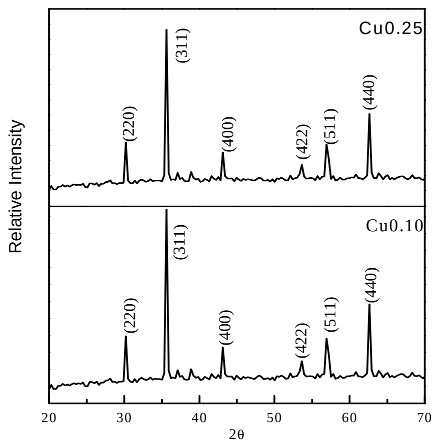

Fig.1. Typical XRD for the compositions x = 0.10 and 0.25

Table 1: Composition variation of density, Seebeck coefficient α, Curie transition temperature T_c, Seebeck coefficient transition temperature T_s and Fermi energy E_F

x	Density (gm/cm³)	Seebeck Coefficient α at room temperature (µV/°C)	Curie Transition Temperature T_c (°C)	Seebeck Coefficient Transition Temperature T_s (°C)	Fermi Energy E_F at 0 K (eV)
0.05	4.3557	-95.831	70	180	-0.782
0.10	4.555	-1860	90	150	-0.5
0.15	4.5479	-1098	110	125	-0.048
0.20	4.6623	-121	120	110	-0.597
0.25	4.9376	-170	130	90	-0.011
0.30	5.5195	-109	140	70	0.019

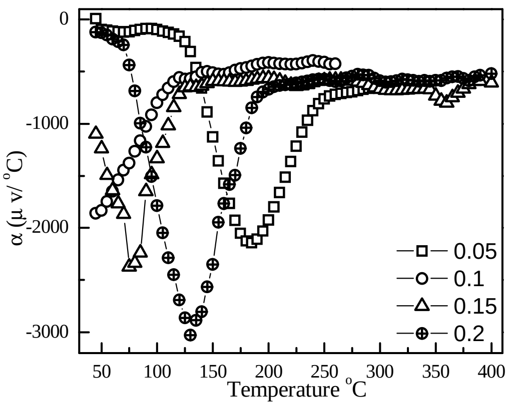

Fig. 2(a). Temperature dependence of Seebeck coefficient of MgCuZn ferrite series

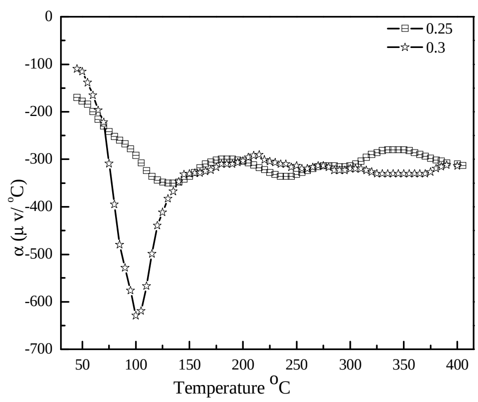

Fig. 2(b). Temperature dependence of Seebeck coefficient of MgCuZn ferrite series

The variation of Seebeck coefficient α with temperature is shown in Fig**.** 2(a) and 2(b). As is observed all the samples exhibited n-type carrier conduction throughout the studied temperature range. These results are in agreement with the data reported in literature [3]. Similar negative Seebeck coefficients were observed for Mn-Mg ferrites [14] and Ti substituted LiMg ferrites[15]. In the present ferrite series the observed thermo emf increases with increase in temperature till certain temperature and then decreases. The temperatures at which these maxima are obtained in Seebeck coefficient was designated as Seebeck coefficient transition temperature T_s by Devender Reddy et al [14] and Ravinder [16]. They also reported that this Seebeck coefficient transition temperature T_s is matching with the magnetic Curie transition temperature T_c of the ferrites.The Curie transition temperature obtained from initial permeability studies for the present series is included for comparison. The compositional variation of the maximum of Seebeck coefficient T_s and that of Curie transition temperature T_c are tabulated in Table1. It may be pointed out here that the trends of T_s and T_c with increasing Cu concentration are altogether different. This clearly signifies that the decrease in Seebeck Coefficient from T_s is not due to magnetic ordering of the ferrites. The probable reason for T_s existence must be due to the conduction mechanism suggested here under.

It is well known that conduction in low mobility ferrite semiconductor is mostly due to Verwey de Boer model [17]. The model suggests a mechanism where charge carriers hop between the cations of same element having multiple valence states. Patil et. al, and others [5, 18, 19] also reported such cup like minima in NiMgZnCo, NiCu and Nb^{4+} substituted MnZn ferrite systems. Though Seebeck coefficient is negative throughout the studied temperature region, the decrease in (negativity of) Seebeck coefficient after T_s must be due to generation of holes at high temperatures. The hole conduction by hopping between Cu^{2+} and Cu^+ according to

$$Cu^{2+} \leftrightarrow Cu^{+} + e^{+} \qquad (1)$$

is the most possible mechanism at high temperatures due to reduction of Cu^{2+} to Cu^+. Similarly the electron hopping mechanism can be represented by

$$Fe^{3+} + e^{-} \leftrightarrow Fe^{2+} \qquad (2)$$

In the present system of ferrites, up to the temperature T_s electron hopping is dominant. Thermal activation of charge carriers increase the mobility of charge carriers resulting in gradual increase of Seebeck coefficient. From T_s hole generation starts according to eqn.(1). Simultaneous electron and hole conduction resulted in decrease of Seebeck coefficient from T_s onwards.

The Fermi energies of the mixed MgCuZn ferrites are calculated from the relation [3, 6]

$$E_F = e\alpha T \_ AkT \qquad (3)$$

where A is a dimensionless quantity having values A=0 and A=2 for ferrites and other terms represent their usual meaning. E_f at various temperatures with A=0 and A=2 are plotted and the extrapolation from these two plots meets on the Y-axis at 0 K. The intercept of Y-axis gives the Fermi level of the system at absolute zero temperature. The corresponding E_f values for all the samples are mentioned in Table 1.

Conclusions:

MgCuZn ferrite series of stoichiometric proportion $Mg_{0.5-x}Cu_xZn_{0.5}Fe_2O_4$ (x = 0.05 – 0.3) are synthesized by usual ceramic double sintering method. Measured Seebeck coefficient increases with increase in Cu till x=0.1 and then decreases. This is attributed to the critical concentration limit of copper. N-type carrier hopping is observed from Seebeck coefficient throughout the temperature range investigated. The Seebeck coefficient transition temperature T_s do not match with magnetic Curie transition temperature but signifies the initiation of hole conduction from T_s.

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