Conduction mechanism in Sn^{4+} substituted copper ferrite

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Abstract. Thermoelectric power (α) and electrical resistivity (ρ) are reported for the system $\text{Cu}_{1+x}\text{Sn}_x\text{Fe}_{2-2x}\text{O}_4$ (where $x = 0.05, 0.1, 0.15, 0.2$ and 0.3) from room temperature to 800 K. The compositions with $x = 0.05$ and 0.2 exhibit n -type conduction while the compositions with $x = 0.1$ and 0.15 show p - to n -type conduction change after 423 K. The conduction at low temperature (i.e. < 400 K) is due to impurities, while at higher temperature (i.e. > 400 K), it is due to polaron. Hopping conduction phenomenon for the present system has been explained on the basis of localized model of electrons. Additional localization may arise due to $\text{Sn}^{4+} + \text{Fe}^{2+}$ stable pairs at B-site and $\text{Cu}^{1+} + \text{Fe}^{3+}$ pair at A-site.

Keywords.

1. Introduction

Unusual thermal, magnetic and dielectric properties of Cu^{2+} ferrite and Cu^{2+} containing ferrites have been reported (Nanba and Kabayashi 1978; Rezlescu and Rezlescu 1974; Patil 1981). In general, they have been attributed to the Jahn–Teller distortion occurring under certain conditions due to Cu^{2+} ions in these ferrites. Phase transition from tetragonal to cubic has been reported at certain critical temperature and composition (Otari *et al* 1990). Recently, we reported structural and magnetic studies on tetravalent substituted copper ferrite (Patil *et al* 1993). However, no information is available on the electrical properties of these materials. We report here the effect of Sn^{4+} substitution in Cu-ferrite on the conduction mechanism.

2. Experimental

The samples with compositions $\text{Cu}_{1+x}\text{Sn}_x\text{Fe}_{2-2x}\text{O}_4$ (where $x = 0.05, 0.1, 0.15, 0.2$ and 0.3) were prepared by a standard ceramic method using AR grade oxides of CuO, SnO_2 and Fe_2O_3 . During this preparation presintering at 600°C for 8 h and powdering of the formed products was followed by final sintering at 950°C for 20 h and furnace cooling at a rate of 80°C per hour. The completion of the solid state reaction was confirmed by X-ray diffraction studies carried out using a Phillips PM 9920 X-ray diffractometer with Fe-K_α radiation. All the samples were found to have densities higher than 95% of their X-ray density.

D.C. resistivity as a function of temperature was measured in the range 300 K to 800 K by two-probe method. Silver paste was applied to obtain good ohmic contacts. The pellet was held tightly in the sample holder. A constant low voltage was applied across the sample and current through the sample was measured. The whole assembly was kept in the regulated furnace and the temperature of the furnace was measured using a Cromel–Alumel thermocouple.

For thermoelectric power measurements a temperature difference $\Delta T = 20$ K was maintained across the pellet with a microfurnace fitted to the sample holder assembly. Temperatures of both the surfaces of the pellet were measured with a Cromel–Alumel thermocouple.

3. Results and discussion

The temperature variation of resistivity (ρ) of all the samples is shown in figure 1. Since the ferrites are semiconductors, their resistivity obeys the relation

$$\rho = \rho_0 \exp(\Delta E/kT).$$

The values of activation energy (ΔE) are estimated by using this relation (table 1). The transition temperatures at which slopes of the plots change are also noted in the same table. From figure 1 it is observed that there are four regions of temperature for each sample. The different regions with changing slopes have been observed from conductivity studies in Cu-containing ferrites (Otari *et al* 1990; Patil *et al* 1992). This is attributed to change in conductivity mechanism. The conductivity mechanism at low temperature is due to impurities, above Curie temperature it is due to magnetic ordering, and at intermediate temperature it is due to phase transition.

The temperature dependence Seebeck coefficient (α) for all the samples is shown in figure 2. All the samples show a cusp-like minimum near the Curie temperature.

Figure 1. Temperature variation of D.C. resistivity (ρ) for $\text{Cu}_{1+x}\text{Sn}_x\text{Fe}_{2-2x}\text{O}_4$ system.

Table 1. Data on activation energy (ΔE) from resistivity. Activation energy from mobility for $\text{Cu}_{1+x}\text{Sn}_x\text{Fe}_{2-2x}\text{O}_4$ system.

Content (x)	Activation energy from figure 1		Activation energy from mobility $\Delta E(\text{eV})$	Transition temperature	
	$\Delta E_1(\text{eV})$	$\Delta E_2(\text{eV})$		Tetra-to cubic $T_1(\text{K})$	Near curie $T_2(\text{K})$
0.05	0.51	0.88	0.82	540	670
0.1	0.48	0.78	0.76	507	646
0.15	0.42	0.63	0.67	476	640
0.2	0.549	0.72	0.71	526	632
0.3	0.62	0.80	—	537	625

Figure 2. Temperature variation of thermo emf (α) for $\text{Cu}_{1+x}\text{Sn}_x\text{Fe}_{2-2x}\text{O}_4$ system.

The samples $x = 0.05$ and 0.2 exhibit n -type conduction from room temperature to 800 K . The compositions 0.1 and 0.15 initially exhibit p -type conduction up to 423 K and n -type conduction above 423 K to 800 K . The results show that the majority of charge carriers are electrons for all the samples. The change in sign of α and variation of α with temperature indicate that the sample contains acceptor and donor centres with different relative predominance. The formation of both types of centres results from the loss of oxygen during sintering. It is also known that substitution of Sn^{4+} ions increases Fe^{2+} content. Both these processes may lead to formation of small amount of Fe^{2+} and Cu^{1+} ions in the sample. The cusp-like minimum may be due to filling up of oxygen vacancies and migration of ions from one site to the other, thereby reducing the concentration of mobile electrons.

Figure 3. Temperature variation of mobility (μ_d) for $\text{Cu}_{1+x}\text{Sn}_x\text{Fe}_{2-2x}\text{O}_4$ system.

The activation energy ΔE_2 calculated by conductivity (ρ) data above 400 K is greater than 0.5 eV, which is much larger than the ionization energy E_i (0.1 eV) for donor or acceptor and $\text{Fe}^{2+}-\text{Fe}^{3+}$ transition energy (0.2 eV), and hence the possibility of band-type conduction is ruled out. The activation energies strongly predict that small polaron conduction dominates. The existence of small polaron and polaron hopping in ferrites has been confirmed by many workers (Vishwanathan and Moorthy 1990). The presence of narrow 3d bands ($\text{Cu}-3d^9$) in these compounds also facilitates small polaron formation. The interaction between excess charge carriers (electrons or holes) present in the narrow band and lattice ions results in the distortion of the lattice, thus producing a potential well deep enough to trap the charge carriers.

The drift mobility (μ_d) was calculated using the results for both ρ and α . The results of these calculations are shown in figure 3. From these results we find that μ_d increases exponentially with temperature according to

$$\mu_d = \mu_0 \exp(-E_d/kT).$$

The calculated values of μ_d , E_d and the temperature dependence of both ρ and α suggest that charge carriers in our sample can be described by the localized model of conduction in ferrites. According to localized model, the electrons are strongly localized on the cations. The localization may be attributed to the electron-phonon interaction or strong magnetic interaction between carriers and magnetic sublattice (Eatah *et al* 1987). An additional localization of Fe^{2+} ions may arise from the inhomogeneous distribution of ions over octahedral and tetrahedral sites in the spinel lattice.

In the present system the additional localization may be due to stable pairs of $\text{Sn}^{4+} + \text{Fe}^{2+}$ at B site and $\text{Cu}^{1+} + \text{Fe}^{3+}$ at A site.

Tetragonal to cubic phase transitions have been observed by many workers in CuFe_2O_4 (Murthy *et al* 1987). The present samples have tetragonal structure and exhibit tetragonal to cubic structural change at temperature T_1 . A phase transition at this temperature is also indicated by sharp decrease in resistivity and abrupt change in activation energy.

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