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FABRICATION AND CHARACTERIZATION OF W-TYPE HEXA-FERRITES

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Abstract

W-type Hexagonal ferrites $BaCu_{2-x}Zn_xFe_{16}O_{27}$ (x = 0.0, 0.5, 1.0, 1.5, 2.0) were prepared by co-precipitation technique. The samples were characterized by on the basis of electrical properties. By measuring electrical resistivity and thermopower the conduction in these materials is attributed to the hopping mechanism of electrons between Fe^{+2} and Fe^{+3} along with holes transfer between Zn^{+2} and Zn^{+3}. The thermoelectric power results show that all these samples are degenerate type semiconductors.

Keywords: Co-precipitation, hexa-ferrites, thermopower, resistivity.

INTRODUCTION

The properties of ferrites have been the subject of extensive investigations because they have paved the way for the development of a wide variety of applications from microwave to radio frequencies. The electrical properties of hexa-ferrites are important due to their applications at high frequencies. Abo El Ata *et al.* [1999] have reported the electrical properties of W-type hexa-ferrites $BaCo_{2-x}Ni_xFe_{16}O_{27}$. The results of thermoelectric power and dc electrical conductivity suggested that the conduction mechanism in this system is due to the hopping of electron between Fe^{+2} and Fe^{+3} along with the hole transfer between Ni^{2+} and Ni^{+3}. It was found that the conductivity increases by the replacement of Co^{+2} by Ni^{+2} ions. A series of polycrystalline $BaCo_{2x}Zn_xFe_{12-2x}O_{19}$ samples prepared by the conventional ceramic method (double sintering process) have been studied [Abo Elata 1998]. The temperature dependence of the thermoelectric power reveals that conduction at low temperatures is due to hopping of electrons between equivalent octahedral sites, where as at high temperatures the probability that conduction process by holes is dominated. The values of the activation energies calculated from the dc conductivity suggested that the hopping process due to small polaron is more probable in $Cu_{1-x}Zn_xFe_2O_4$ ferrites prepared by ceramic technique [Abbas *et al.* 1995]. It was also observed that the resistivity increases with increasing Zn concentration. The sharp increase of the electrical resistivity with the Zn concentration near the stoichiometric $Cu_{0.9}Zn_{0.1}Fe_2O_4$ was attributed to the change of species of charge carriers from n-type at low Zn concentration to p-type at higher Zn concentration. It was also observed that with the increase of Zn concentration, activation energy increases, this fact was attributed to the creation of more cations and deficiency of oxygen vacancies which might have been produced due to a rise in temperature and loss in zinc. It was observed that the concentration of oxygen vacancies was an important factor in electrical resistivity. Patil *et al.* [1994] have reported electrical resistivity and Seebeck coefficient for Ni-Cd ferrites as a function of temperature. From diffraction analysis it was reported that all the samples were single phase. The lattice constant was observed to increase with the increase of Cd-content. This was in accordance with the large ionic radius of Cd (1.03Å) as compare to that of Ni (0.78 Å). The activation energies found in ferri region (< 400 K) were < 0.3eV and in para region (> 400K) were > 0.45 eV. It was observed that for all the compositions the thermopower coefficient (α) was negative over the whole range of temperature, indicating that the charge carriers were electrons. Titanium substituted magnesium ferrites having the compositional formula $Mg_{1+x}Ti_xFe_{2-2x}O_4$ prepared by the solid state reaction method have been reported by [Purushotham *et al.* 1993]. It was seen that the sign of the (α) for all the samples were negative, indicating that the predominant conduction mechanism in these ferrites was hopping of electrons from Fe^{+2} to Fe^{+3} on octahedral sites. The room temperature conductivity values are found to range from 10^{-7} to 10^{-4} ohm^{-1} cm^{-1}. Electrical properties of $Ni_{0.65}Zn_{0.35}Cu_xFe_{2-x}O_4$ ferrites have also been studied by Henish *et al.* [1991]. The low activation energy at x = 0.4 was observed to cause pronounced increase in the d.c. conductivity. The increase in conductivity at elevated temperature was reported to be due to the generation of more positive charge carriers. The decrease in the activation energy by Cu addition was due to the fact that the introduction of Cu^{+2} into the lattice creates lattice vacancies. Since the valency of Cu^{+2} is less than the valency of Fe^{+3}, more oxygen vacancies will be formed, which gave rise to conductivity and decrease the activation energy. For further addition of Cu (x >0.4), the increase in the activation energy and the decrease in the conductivity was attributed to the creation of more cations which reduce oxygen vacancies. It was also observed that the compositions containing Cu additives have positive values of the (α).

In the present study $BaCu_{2-x}Zn_xFe_{16}O_{27}$ (x = 0.0, 0.5, 1.0, 1.5, 2.0) W-type hexagonal ferrites were prepared by co-precipitation technique and were characterized by the electrical measurements.

MATERIALS AND METHODS

$BaCu_{2-x}Zn_xFe_{16}O_{27}$ (x = 0.0, 0.5, 1.0, 1.5, 2.0) W-type hexagonal ferrites were prepared by co-precipitation technique. The starting materials were metal chlorides. The metal chlorides used in the preparation were of reagent grade. The chemical formulae for each constituent used are given by:

Barium Chloride dihydrate $BaCl_2.2H_2O$, Copper Chloride dehydrate $CuCl_2.2H_2O$, Zinc Chloride $ZnCl_2$, Ferric Chloride hexahydrate $FeCl_3.6H_2O$, where as NaOH and Na_2CO_3 were used as precipitating agents.

The metal chlorides were weighed using Sartorius electronic balance having an accuracy of 10^{-4} gm. The $BaCl_2.2H_2O$, $CuCl_2.2H_2O$, $ZnCl_2$ and $FeCl_3.6H_2O$ were mixed in an appropriate proportion using following chemical reaction:

$$BaCl_2.2H_2O + (2\text{-}x)\ CuCl_2.2H_2O + x\ ZnCl_2 + 16\ FeCl_3.6H_2O \rightarrow BaCu_{2\text{-}x}Zn_xFe_{16}O_{27}$$

where x = 0, 0.5, 1.0, 1.5, 2.0. Metal chlorides with stoichiometric composition of $BaCu_{2\text{-}x}Zn_xFe_{16}O_{27}$ were mixed in 25ml of distilled water and stirred constantly with the help of magnetic stirrer until a homogeneous solution was obtained. These metal chlorides were present in the solution in a stoichiometric ratio of (1:2:16). The precipitating agent was prepared by mixing NaOH and Na_2CO_3 in 100ml of distilled water. The weights of NaOH and Na_2CO_3 for each sample were 1.75 gm and 4.5 gm respectively, to ensure the PH value higher than 10, required for the chemical reaction to take place. Dilute precipitated solution was used for the formation of uniform precipitates. The precipitating agent was added slowly until the co-precipitation occurs. When the precipitation completed, the solution was then thoroughly washed with distilled water for several times until the removal of NaCl is confirmed. Adding the last drop of washing from the beaker into $AgNO_3$, confirmed the removal of NaCl, by precipitation technique. If no precipitation occurs that confirms the removal of NaCl.

The solution was then filtered with the help of suction flask operating on a water pump. This co-precipitated product contains moisture along with carbonates and hydroxides ions. This co-precipitated product was dried in an electric oven at a temperature of 110 °C for 12 hrs. The removal of these ions and carbonates is done by the heat treatment.

The dried powder was mixed homogeneously in an agate mortar by grinding the constituents for two hours. Before and after this process the mortar and pestle were rinsed with acetone. The finally ground powder was then pelletized under the load of 30 KN using hydraulic pressing machine (PAUL-OTTOWEBER). The pellets were first annealed at 600°C for three hours, and then at 800°C for 18 hours. At 800°C all the carbonates, hydroxides and moisture is removed. After this heat treatment the pellets were annealed at 1000°C for 24 hours. Final sintering was done at 1300°C for three hours. After each heat treatment, the samples were quenched in air to obtain the equilibrium position of the cations.

Two-probe technique was used for dc resistivity measurements. Before the measurement of electrical resistivity, both sides of the samples were polished to remove oxide layers formed during sintering and to remove scratches from their surfaces. A sample holder with pressure contact electrodes made up of copper was used. The copper leads were used for electrical connections. A dc power supply model I P-2717 HEATKIT and a very sensitive electrometer model 610C (Keithley) were connected in a series with the sample holder. The current voltage data was taken using above mentioned power supply and electrometer. Thermopower was measured by differential technique as reported by [Islam *et al.* 2002]. Two probes made up of Cu were used to measure the thermal emf across the sample. Heater wire was wound separately on both electrodes that were heated independently. Two separate chromel-alumel thermo-couples were used in order to measure the temperature difference across the sample.

RESULTS AND DISCUSSION

The current-voltage characteristics of $BaCu_{2-x}Zn_xFe_{16}O_{27}$ hexa-ferrites for x = 0, 0.5, 1.0, 1.5, 2.0 are plotted in Fig. 1. From the slope of each line in Fig. 1, resistance R was calculated and hence room temperature resistivity (ρ) by using the formula: $\rho=RA/t$, where A is the area of electrode in contact with the sample and t is the thickness of the sample. Logarithm of room temperature resistivity (ρ) has been plotted against the concentration (x) as shown in Fig. 2. It can be observed that as Zn concentration increases, the resistivity first decreases to a minimum at x = 0.5, this may be attributed to the production of Fe^{+2} ions in the spinel blocks and the increases in the resistivity at x > 0.5 may be due to hindrance of the hopping mechanism between Fe^{2+} and Fe^{3+} along with the hole transfer between Zn^{2+} and Zn^{+3}.

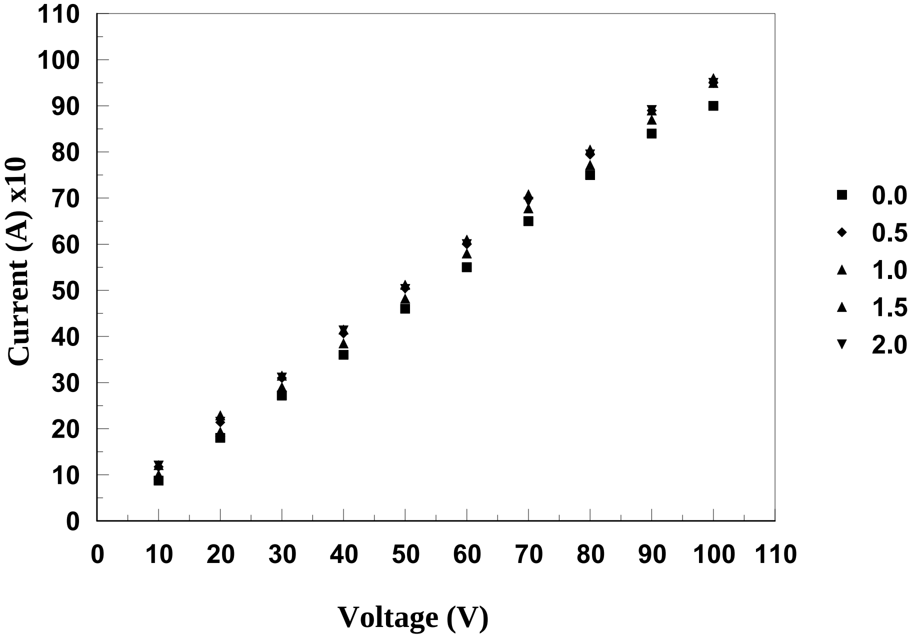

Fig. 1: Current voltage characteristics of $BaCu_{2-x}Zn_xFe_{16}O_{27}$ hexagonal ferrites (x = 0.0, 0.5, 1.0, 1.5, 2.0).

Fig. 3 shows the temperature dependence of thermoelectric power coefficient (α) for all the samples in the temperature range 25-225°C for the $BaCu_{2-x}Zn_xFe_{16}O_{27}$ system. It can be seen that □remains positive throughout the temperature range for the samples (x = 0.0, 0.5, 1.0). The positive values of α show that the dominant conduction mechanism is p-type [Abo El Ata *et al.* 1999, Abo Elata *et al* 1998, Islam *et al.* 2002] and the samples are degenerate type semiconductors. For x =1.5, the α is positive up to 90°C, indicating majority of charge carriers are holes, above 90°C the α is negative showing that the charge carriers are n-type (electrons). For x = 0.5 the α remains negative throughout the temperature range, hence indicating n-type conduction. Since α varies with temperature revealing that all the samples are non-degenerate semiconductors [Abo El Ata *et al.* 1999, Abo Elata *et al.* 1998, Islam *et al.* 2002].

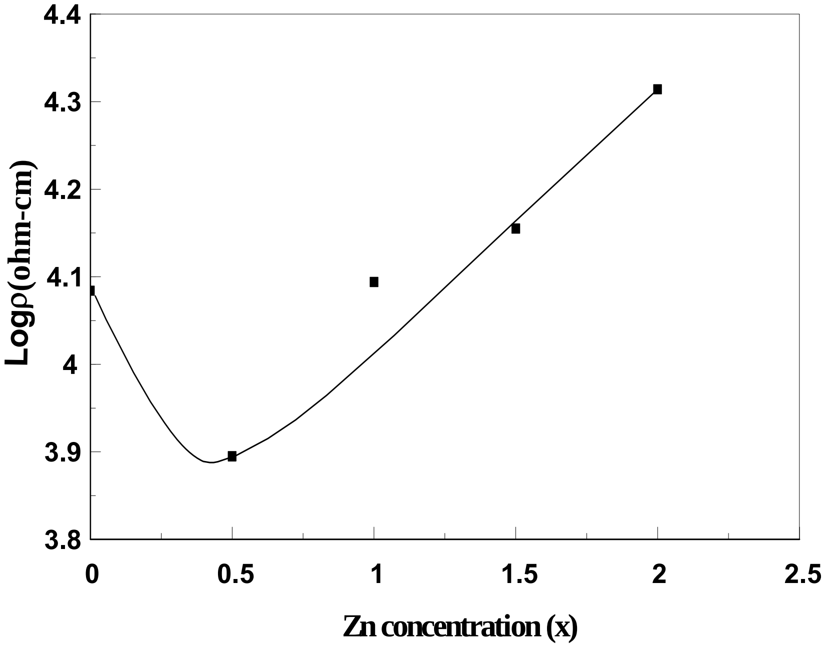

Fig. 2: Room temperature resistivity of $BaCu_{2-x}Zn_xFe_{16}O_{27}$ hexagonal ferrites as a function of Zn concentration (x = 0.0, 0.5, 1.0, 1.5, 2.0).

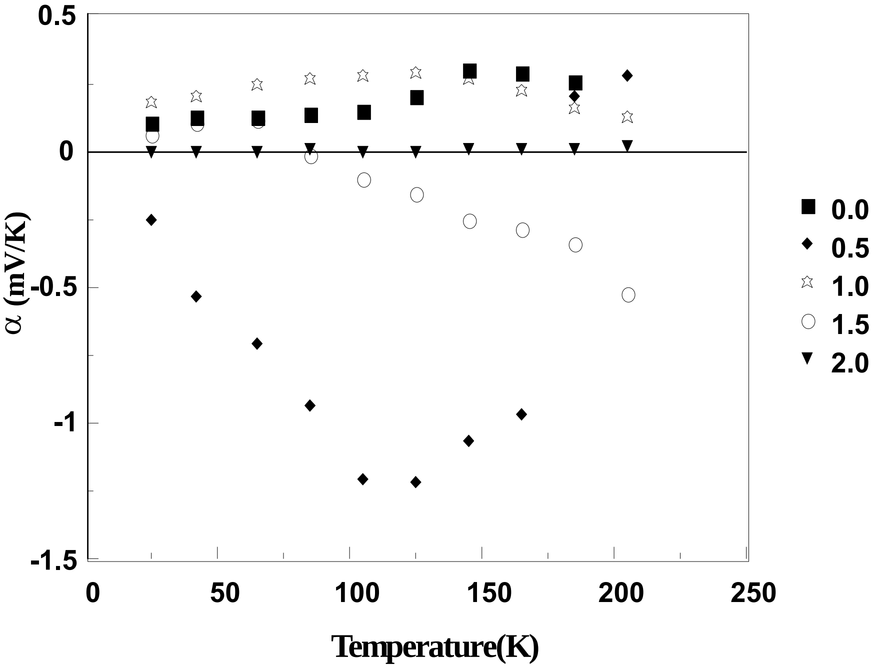

Fig. 3: Plot of thermopower (α) Vs temperature for $BaCu_{2-x}Zn_xFe_{16}O_{27}$ hexagonal ferrites (x = 0.0, 0.5, 1.0, 1.5, 2.0).

CONCLUSIONS

- From electrical resistivity measurements it has been observed that by changing Zn concentration, resistivity initially decreases up to x = 0.5 and then increases by increasing concentration ($x>0.5$), it can be attributed to the hopping of electron between Fe^{+2} and Fe^{+3} ions.
- The variation in thermopower (α) with temperature shows that all the samples are non-degenerate type semiconductors.

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