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Effect of Tb–Mn substitution on DC and AC conductivity of Y-type hexagonal ferrite

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ABSTRACT

Single phase nanostructured Tb–Mn substituted Y-type hexaferrites with nominal composition $Sr_2Co_{2-x}Mn_x\ Tb_yFe_{12-y}O_{22}$ ($x = 0.0$–1, $Y = 0.0$–0.1) were synthesized by the normal microemulsion method. The values of activation energy calculated from DC electrical conductivity increases with the substitution of Tb–Mn suggests that the conduction mechanism in the present ferrite system is polaron hopping. The appearance of broad Debye peaks in imaginary electric modulus plots (m'') show the existence of relaxation process in all these samples. The complex impedance plane plots show a single semicircle, which indicates the capacitive and resistive properties of the materials are due to contribution of grains and grain boundaries in ferrites. It is observed that Tb–Mn Substitution makes comparatively small difference on the grain resistance, but leads to a remarkable rise of grain boundary resistance. High values of quality factor are obtained required for power applications and high frequency multilayer chip inductors.

1. Introduction

Ferrites are very key materials for technological applications [1]. They have been widely used for their excellent magnetic properties [2], e.g. magnetic fluids, hyperthermal cancer treatment, in magnetic resonance imaging (MRI) enhancement, high density magnetic recording and drug delivery, etc. Especially hexa ferrites have attracted much attention over the decade due to their versatile applications [3,4]. Due to development in the field of telecommunication, the operational frequency of electronic devices is rapidly moving to gigahertz frequencies. Polycrystalline hexaferrites, having low AC electrical conductivity and consequently, low eddy currents and dielectric losses, are particularly well suited for use in high-frequency applications. The experimental measurements for electric conduction, thermoelectric power, charge carriers concentration, charge carriers mobility and activation energy give much information on the behavior of the free and localized charge carriers. Their properties are heavily dependent on their structure, composition and ion distribution [5,6]. Gorter made the first attempt to determine the position of the magnetic ions and orientations of the spins in the crystal lattice by considering exchange interactions [7]. It was observed that the spins are collinear in the basal plane particularly in Y-type hexagonal structure. The structure of Y-type hexaferrite has space group (R3m). The Y-type hexagonal ferrites have a crystalline structure built up as a superposition of S and T blocks. The unit cell is composed of the sequence STSTST including three formula units. Each formula unit consists of two layered spinel S block and four-layered antiferromagnetic T block. The metallic cations are distributed among six sub lattices [7]. Therefore, by tailoring the composition and the structure of the Y-type hexaferrite, it is possible to improve the properties required for specific applications. Because of this possibility to tailor the properties of ferrites, they have been synthesized by various methods, including solid state reaction [8], hydrothermal [9], sol–gel [10], sol–gel autocombustion [11], co-precipitation [12], citrate precursor technique [13], thermal plasma [14], pulsed wire discharge [15], etc. In the present work, we have used the normal microemulsion method which is better to obtain the nano-size materials as compared to others. The surfactant used form the micelle which acts as a nanoreactor so the size and shape of particles can be controlled. It is well known that the microemulsion method has been proved to be one of the most effective routes to realize the low temperature sintering of ferrites. The study of DC electrical conductivity, AC conductivity, and drift mobility give much more valuable information on the behavior of free and localized electric charge carriers. This leads to good explanation and understanding of the mechanism of electric conduction in the studied samples. Therefore, the authors aimed to study the effect of temperature and composition on the DC electrical conductivity and drift mobility. Moreover special intention have been on the frequency

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dependent AC conductivity and complex plane plot (Nyqiust plot) for a series of Mn–Tb substituted $Co_2Sr_2Fe_{12}O_{22}$ Y-type hexaferrites.

2. Experimental procedure

2.1. Chemicals

The chemicals of analytical grade were used to synthesize Y-type strontium hexa-ferrites $Sr_2Co_{2-x}Mn_x\,Tb_yFe_{12-y}O_{22}$. The starting materials were $Fe(NO_3)_3{\cdot}9H_2O$ (Riedel-de Haen, 97%), $Co(NO_3)_2{\cdot}6H_2O$ (Merck, >99%), $MnCl_2$. $2H_2O$(Merck, >99%), $Sr(No_3)_2$ (Merck, 99%), Tb_2O_3 (Merck, 99%), (cetyltrimethyl ammonium bromide) CTAB (Merck, 97%) as a surfactant, NH_3 (Fisher Scientific, 35%) as a precipitating agent and methanol (Merck, 99%) as washing agent.

2.2. Synthetic procedure

The Y-type hexaferrite samples with nominal composition $Sr_2Co_{2-x}Mn_x\,Tb_y Fe_{12-y}O_{22}$ ($x = 0.0$–1, $Y = 0.0$–0.1) were prepared by the normal microemsulsion method. The metallic salt solution of the required molarities were prepared in deionized water and mixed in a baker. The CTAB was also added in metals solutions with ratio 1: 1.5 (metals: CTAB). The solution was stirred on the magnetic hot plate at 60 °C until it formed a clear solution. The ammonia solution was added dropwise to form the precipitates. After that the precipitates were washed with deionized water and finally with methanol. Then the precipitates were dried in an oven at 150 °C and finally annealed at 1050 °C for 8 h using box furnace (Heyaius, D-6450 Hanau, Germany).The formation of substituted Y-type hexaferrites from the starting materials can be shown in Scheme 1.

2.3. Characterization

The DC electrical conductivity was obtained by a simple two-probe method within temperature range of 300–573 K. A Keithly source meter model-197 was used for the said purpose. The DC conductivity was calculated by using the formula

$$\sigma_{DC} = d/RA \tag{1}$$

where R is the resistance, d is the thickness of the sample and A is area of electrode.

Drift mobility, μ_d of all the samples were calculated using the relation.

$$\mu_d = \sigma_{DC}/ne \tag{2}$$

where e is the charge of electron, σ_{DC} is conductivity and n is the concentration of charge carrier and can be calculated from the well-known equation:

$$n = N_A d_b P_{Fe}/M \tag{3}$$

where N_A is the Avogadro's number, d_b is the measured bulk density of sample, P_{Fe} is the number of iron atoms in the chemical formula of the ferrites and M is the molecular weight of the samples.

Dielectric data and Impedance was measured on a Agilent impedance analyzer model E4991ARF. The AC conductivity was calculated from dielectric constant and dielectric loss tangent ($\tan\delta$) as

$$\sigma_{AC} = 2\pi f \varepsilon_o \acute{\varepsilon} \tan\delta \tag{4}$$

where σ_{AC} is the AC conductivity and f is the frequency, π and ε_o are constants.

Impedance measurements were performed in the frequency range from 1 MHz to 3 GHz at room temperature by taking the absolute value of impedance $|Z|$ with varying complex angle θ_Z. The real and imaginary parts of impedance can be written as

$$Z' = R = |Z|\cos\theta_Z \tag{5}$$

$$Z'' = X = |Z|\sin\theta_Z \tag{6}$$

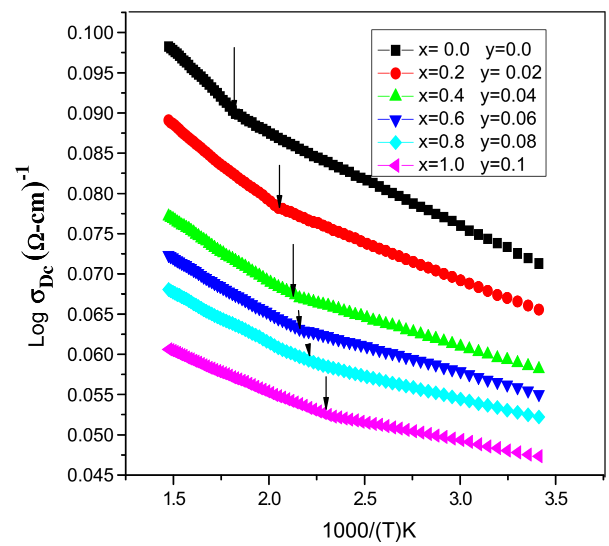

Fig. 1. Change in DC electrical conductivity with temperature for (Tb–Mn) substituted $Co_2Sr_2Fe_{12}O_{22}$ hexa ferrites.

The real and imaginary parts of the electrical modulus, M' and M'' respectively they can be calculated as fallows [16]:

$$M' = \varepsilon'/\{(\varepsilon')^2 + (\varepsilon'')^2\} \tag{7}$$

$$M'' = \varepsilon''/\{(\varepsilon')^2 + (\varepsilon'')^2\} \tag{8}$$

where ε' and ε'' are real and complex parts of permittivity respectively.

3. Results and discussion

3.1. DC conductivity

The relation between electrical conductivity and temperature [11] may be expressed as

$$\sigma = \sigma_0 \exp \Delta E/dBT \tag{9}$$

where σ is DC conductivity, ΔE is the activation energy in (eV) for conduction, k_B is the Boltzmann constant and T is the temperature in Kelvin (K). Fig. 1 describes DC electrical conductivity versus temperature ($10^3/T$) from room temperature up to about 678 K. The conductivity behavior for all samples is analogous with each other. The conductivity increases with increasing temperature, indicating the semiconductor behavior of the samples [17–19]. Deep observation of DC conductivity curves shows two distinct regions. This behavior of different regions was examined before for Y-hexaferrite [20] and spinal ferrite [21]. First region appears in ferrite at low temperatures. Low activation energies of first region suggest that the conduction in this region may be due to the free charge carriers

$$Tb_2O_3 + HNO_3 \rightarrow Tb(NO_3)_{3aq} + H_2O$$

$$(12\text{-}y)Fe(NO_3)_{3(aq)} + Sr(NO_3)_{2(aq)} + 2\text{-}xCo(NO_3)_2 + xMnCl_{2(aq)} + yTb(NO_3)aq + NH_4OH$$

$$\downarrow$$

$$Sr(OH)_2\ 12\text{-}yFe(OH)_3\ 2\text{-}xCo(OH)_2\ xMn(OH)_2\ yTb(OH)_3 + NH_4NO_3 + NH_4Cl + H_2O$$

$$\downarrow 1050\,□C$$

$$Sr_2Co_{2-x}Mn_x\,Tb_yFe_{12-y}O_{22}$$

Scheme 1. Formation of Tb–Mn substituted Y-type hexaferrites from their starting materials.