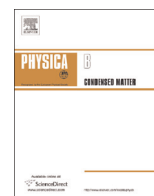




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The electrical properties of manganese ferrite powders prepared by two different methods



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ABSTRACT

Two powder samples of manganese ferrite (MnFe_2O_4) with different morphology and particle size 30–40 nm, denoted by A and B have been synthesized by different methods starting from $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$. Sample A was obtained by co-precipitation followed by calcination at 900 °C and sample B has been obtained by hydrothermal method. XRD analysis show that calcination leads to the occurrence of other phases than MnFe_2O_4 , therefore the hydrothermal method gives better results.

From the temperature dependence of the electrical resistivity, measured over the range 300–483 K, the activation energy, ΔE , of the investigated samples has been evaluated, resulting in 0.43 eV (for sample A) and 0.32 eV (for sample B).

The conductivity mechanism in the samples was explained in terms of Mott's variable range hopping (VRH) model. The results showed that the density of states at the Fermi level is constant over the investigated temperature range, being in order of $0.788 \times 10^{17} \text{ eV}^{-1} \text{ cm}^{-3}$ (for sample A) and $2.05 \times 10^{17} \text{ eV}^{-1} \text{ cm}^{-3}$ (for sample B). The hopping distance, R and the hopping energy, W (parameters of VRH model) have also been computed. Room temperature values are $R=27.08 \text{ nm}$ and $W=152 \text{ meV}$ for sample A and $R=21.29 \text{ nm}$ and $W=120 \text{ meV}$ for sample B.

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1. Introduction

The manganese ferrite with spinel structure and chemical formula MnFe_2O_4 belongs to the family of MeFe_2O_4 type oxides (where $\text{Me}=\text{Mn}, \text{Co}, \text{Zn}, \text{Mg}, \text{etc.}$), which have a great applicative importance [1].

Manganese ferrite nanoparticles have drawn the attention of researchers due to the high value of the magnetic susceptibility compared to other ferrite nanoparticles and various possible applications of manganese ferrite have been proposed. In Refs. [2–4], the use of manganese ferrite nanoparticles as ultrasensitive magnetic resonance imaging (MRI) probe and magnetic drug targeting has been suggested. Also, the manganese ferrite particles have been synthesized for their use in hyperthermia applications [5].

The obtaining of materials with electromagnetic absorbent properties is another applicative area, in which the utility of MnFe_2O_4 nanoparticles was proven [6,7].

Ferrite compounds, in the form of a thin film of nickel manganese ferrite nanoparticles or cobalt manganese ferrite nanoparticles were found to be useful as gas sensors [8,9].

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In the preparation of ferrofluids, the most usual material used is magnetite (Fe_3O_4) [10], but to obtain ferrofluids with controllable physical properties, some mixed ferrite particles of type Mn–Zn or Mn–Fe can be used [11].

The electrical properties of ferrites are related to the distribution of cations between tetrahedral and octahedral positions of the crystal lattice and depend on their composition and microstructure, conditions and method of synthesis [12,13].

In the case of ferrites, the cations are surrounded by oxygen anions and to a first approximation they can be considered as isolated from each other. As a result, the model of localized states is more appropriate for ferrites than the band model of electrons. Conduction in ferrites is related to the direct electronic exchange between Fe^{2+} and M^{3+} ions (M denotes metal ions). The diffusion of d electrons from one localized state to another is possible only when their energy is larger than a minimum value, called activation energy [13,14].

In various research studies, using different calcination temperatures and different molar ratios of raw materials, the manganese ferrite was obtained starting from $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ [1,15] or using $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as reactants [12,16]. In the present paper, in the obtaining of manganese ferrite nanoparticles, $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ have been used. Using these raw materials, two samples have been

synthesized by co-precipitation and hydrothermal methods.

The dependence on temperature, T , of the electrical resistivity, ρ , of these two samples has been measured in order to study the effect of the obtaining method on the electrical properties of the manganese ferrite powders. The static conductivity mechanism in samples was explained using Mott's variable range hopping (VRH) model and the activation energy (ΔE) as well as different related parameters were computed.

2. Samples

2.1. Obtaining methods

Sample A was obtained by co-precipitation followed by calcination at 900 °C. The starting materials were MnCl_2 and FeCl_3 in aqueous solution (0.945 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ mixed with 2.705 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$). Given the high reactivity of manganese ions in chemical reactions, the iron content of initial chlorides is slightly larger than the stoichiometric ratio of ions in MnFe_2O_4 [17]. Subsequently, 2 M NaOH aqueous solutions were added with constant stirring to the above solution until $\text{pH}=11$ were reached. After adding NaOH, magnetic stirring was done for 2 h at a temperature between 80 and 90 °C. After filtering, the precipitate was washed several times with distilled water to remove chlorides until the resulted water solution reached $\text{pH}=7$. Finally, the washed precipitate was calcined at the temperature of 900 °C for four hours.

Sample B was obtained by hydrothermal method. The starting materials were 0.945 g $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ and 2.705 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in aqueous solution and the precipitation was done with 2 M NaOH aqueous solution, at $\text{pH}=11$ (as in the case of sample A). The mixture was introduced into a Morey-type autoclave and maintained at a temperature of 250 °C, for 12 h. After decantation and filtration, the resulting precipitate was washed with distilled water on a filter paper and then laid out to dry in an air oven, at 80 °C, resulting in a powder sample.

2.2. Structural and morphologic characterization

The crystalline structure of the prepared samples was investigated by X-ray diffraction (XRD) using a PANalytical-X'Pert PRO MRD diffractometer. Powder morphology was observed using a PANalytical scanning electron microscope (SEM). The elemental analysis was analyzed through EDX facility of SEM.

The XRD patterns of the investigated samples are presented in Fig. 1. Based on the XRD pattern of samples one can assert that

sample A (Fig. 1(a)) consists of a mixture of MnFe_2O_4 , FeMnO_3 , Mn_2O_7 and Fe_2O_3 . As reported in Ref. [18], at elevated temperatures, MnFe_2O_4 is unstable in air and on the surface of ferrite particles, Mn^{2+} ions oxidize to form Mn^{3+} , leading to dissociation of MnFe_2O_4 and occurrence of other phases. Therefore, any preparation method which involves calcination step is not suitable for the preparation of manganese ferrite nano-particles.

Fig. 1(b) shows the XRD pattern of sample B and it contains peaks that match to the standard data of the cubic spinel MnFe_2O_4 (JCPDS Card no. 75-0034). The XRD pattern does not contain extra peaks, indicating formation of MnFe_2O_4 as single phase [19]. The Scherrer formula [20] was used in order to calculate the average size of MnFe_2O_4 crystallites of both samples. The values obtained are approximately of 37.93 nm for sample A and 31.9 nm for sample B.

Fig. 2(a) and (c) show the morphology of MnFe_2O_4 powder samples. From the SEM photograph (Fig. 2(a)) it is observed that sample A (obtained by co-precipitation) consists of polycrystalline grains with average size of 200–300 nm. It can also be seen in Fig. 2(c) that sample B also contains polycrystalline grains with average size of a few hundred nanometers.

The results of EDX (which is a semi-quantitative analysis) are presented in a graphical form in Fig. 2(b) and (d) and confirm that both ferrite samples consist of Mn, Fe and O. The atomic ratio of elements, 1:2.04:3.81 (for sample A) and 1:1.90:3.42 (for sample B) are close to the ratio of MnFe_2O_4 formula.

3. Results and discussions

For measurements of the electrical resistance, R , of samples at various temperatures, T , over the range 30–200 °C, a laboratory made experimental setup (whose schematic representation is shown in Fig. 3) has been used.

As can be seen from Fig. 3, the ferrite powder sample (1) was inserted into an electric furnace (3), which is heated by means of an electrical resistance connected to a voltage source, u . The sample (1) is in contact with two electrodes (2), which are connected to an ohmmeter, (Ω). The ends of the furnace are insulated with two thermo-insulating material stoppers (5) and the temperature T of the sample was measured with a thermocouple (4).

The length, L and section, A of the samples had the values: $L = 11 \text{ mm}$ and $A = \pi D^2/4 = 11.34 \text{ mm}^2$, where $D = 3.8 \text{ mm}$ represents the diameter of the glass tube in which the ferrite sample was introduced.

Based on the experimental values of the electrical resistance of

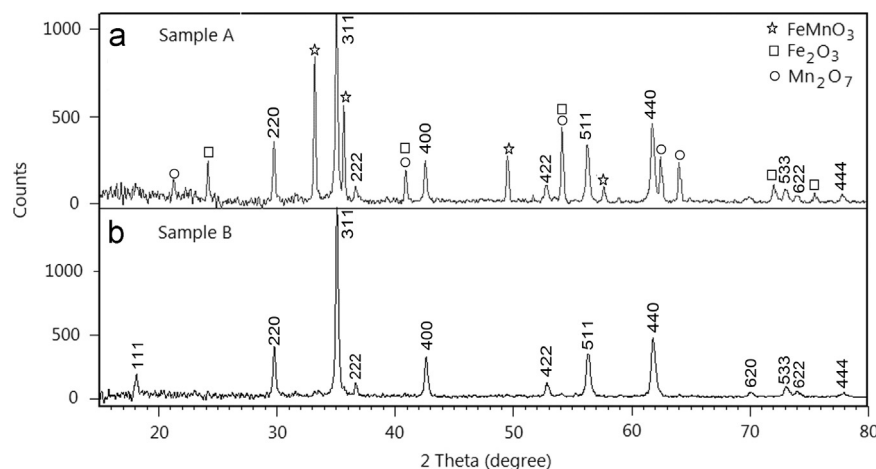


Fig. 1. X-ray diffraction patterns of samples A and B.

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