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Novel Combustion Synthesis of La^{3+}-Substituted $MnFe_2O_4$*

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Abstract—La^{3+}-substituted $MnFe_2O_4$ compounds have been prepared by using a novel combustion synthesis method. This process was found to yield homogeneous, finely crystalline powders without intermediate decomposition and/or calcination steps. Combustion-synthesized powders were sintered at 1000°C, and structural features of thus prepared materials were characterized by XRD analysis and FT-IR spectroscopy. The dc electrical conductivity of synthesized materials has been measured as a function of temperature up to 1000°C. The materials have shown semiconducting behavior at elevated temperatures. The ac electrical conductivity of synthesized samples was found to increase with increasing applied frequency. The dielectric constant and dielectric loss tangent have also been characterized.

Keywords: combustion synthesis, manganese ferrites, semiconductors, electrical properties.

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INTRODUCTION

Mixed metal oxides with a spinel-type structure have been extensively studied by many researchers [1–3] as they exhibit interesting structural, electrical, and magnetic properties [4, 5]. Spinel ferrites are a class of ternary oxides with composition AB_2O_4 wherein the A ions occupy the tetrahedral sites and B ions occupy octahedral sites [6, 7]. The spinel structure consists of a face centered cubic arrangement of oxygen ions. A unit cell contains 32 oxygen ions. A^{2+} cations occupy 64 tetrahedral sites and B^{3+} cations occupy 32 octahedral sites. The distribution of cations between both sites varies between two limiting cases. The physical and chemical properties of spinels not only depend on the type of A and B but also on the distribution of these cations over different crystallographic sites [8]. Properties of ferrites are known to be sensitive to the synthesis method [9]. A small deviation in the stoichiometry of ferrite greatly affects its properties.

The ferrite materials are synthesized by one of two major routes, either by a traditional ceramic heat and beat approach or by wet chemical synthesis [10, 11]. The synthesis technique used to prepare ferrite materials has a strong influence on their magnetic and electrical properties [12]. This variance is a consequence of the microstructure formed by the different synthetic routes. Spinel ferrites are commonly used in many electronic and magnetic devices due to their high magnetic permeability [13] and low magnetic loss [14, 15]. They are also used as electrode materials [16] for high-temperature applications because of their high thermodynamic stability [8], electrical conductivity [17], catalytic activity [18], and resistance to corrosion [1, 19].

Considering the importance of ferrites, in this work we synthesized some La^{3+}-substituted $MnFe_2O_4$ compounds and characterized their structural and electrical properties.

EXPERIMENTAL

La^{3+}-substituted $MnFe_2O_4$ powders were synthesized using a novel combustion synthesis method. Aliquot amounts of analytical grade metal nitrates—$Mn(NO_3)_2 \cdot 6H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, and $La(NO_3)_3$—were mixed with carbamide $CO(NH_2)_2$ and dissolved in deionized water to obtain a precursor solution. The solution was preconcentrated in a quartz crucible until evaporation of free water, after which spontaneous inflammation of dried powder took place. The combustion reaction resulted in formation of black porous ash in the container. This ash was then sintered at 1000°C for 20 h in an electrical furnace. The phase formation and structural features of thus synthesized compounds were characterized by XRD (JEOL 8030 X-ray diffrac-

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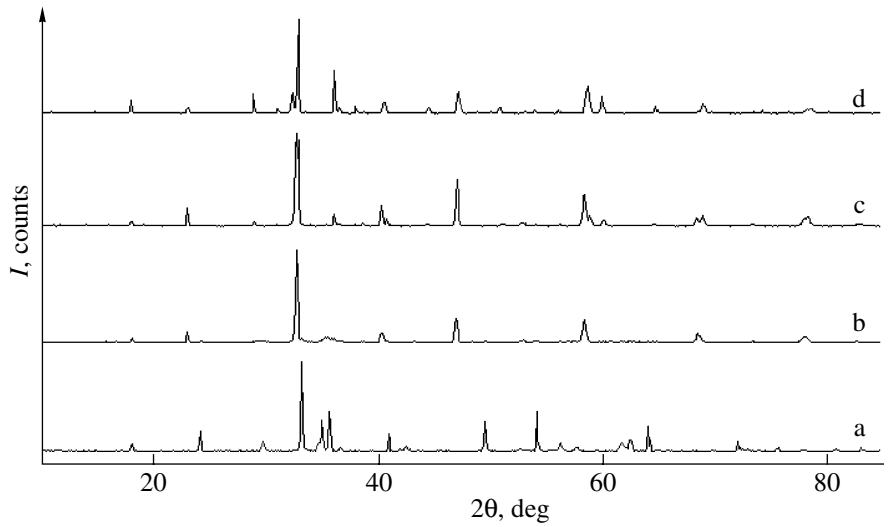

Fig. 1. Diffraction patterns of combustion-synthesized $MnFe_{2-x}La_xO_4$ compounds: $x = 0$ (a), 0.4 (b), 1.6 (c), and 2.0 (c).

tometer, Cu-K_α radiation $\lambda = 1.541$ Å, $2\theta = 10$–$80°$). FT-IR spectra of synthesized samples (in KBr discs) were taken with a Perkin-Elmer Paragon-500 spectrometer in the range 400–1000 cm^{-1}. DC electrical conductivity of sintered specimens was determined (up to 1000°C) by four-probe method.

RESULTS AND DISCUSSION

The XRD patterns of combustion-synthesized $MnFe_{2-x}La_xO_4$ compounds ($x = 0$, 0.4, 1.6, and 2.0) are shown in Fig. 1. The sharp well-defined peaks show the crystalline nature of the synthesized compounds. All the peaks are matched with the characteristic reflections of the parent compound. The lattice constant values as derived from the XRD data are given in Table 1. A change in lattice constant values is mainly due to difference in the ionic radii of metal ions (1.36 Å for La^{3+} and 0.64 Å for Fe^{3+}). The lattice constants are in good agreement with the reported values [7].

Lattice constant a and dc conductivity σ_{dc} of synthesized $MnFe_{2-x}La_xO_4$ compounds

	a, Å	σ_{dc} at 1000°C, S cm^{-1}
$MnFe_2O_4$	8.50	5.6
$MnFe_{1.6}La_{0.4}O_4$	9.0825	14.0
$MnFe_{0.4}La_{1.6}O_4$	9.0825	18.0
$MnLa_2O_4$	8.6093	10.21

The FT-IR spectra of parent $MnFe_2O_4$ is shown in Fig. 2. According to the literature data, the absorption band at 480.3 cm^{-1} can be attributed to tetrahedral complexes while that at 570.82 cm^{-1}, to octahedral ones. The difference in band positions is due to a different Fe^{3+}–O^{2-} separation in the octahedral and tetrahedral complexes. Upon introduction of La^{3+} ions, the bands of tetrahedral site were found to shift toward higher ν (from 570.82 to 618.5 cm^{-1}) due to shortening in the Fe^{3+}–O^{2-} distance.

The dc electrical conductivity (σ_{dc}) of synthesized compounds was found to increase with temperature. This can be associated with the presence of impurity phases. As the temperature increases, the mobility and concentration of charge carriers grow, so that the conductivity steadily increases up to 1000°C. The conductivity markedly grows with increasing concentration of La^{3+} ions. At 1000°C, the maximum conductivity (18 S cm^{-1}) was observed for $MnFe_{0.4}La_{1.6}O_4$ (see Table 1). The results of conductivity measurements were used to draw the Arrhenius plots in the $\log(\sigma_{dc})$ – $1/T$ coordinates (Fig. 3). These plots exhibit three distinct regions with different slopes. Generally, a change in slope is attributed to a change in the mechanism of conduction. Conduction at low temperatures is due to electron hopping between Fe^{2+} and Fe^{3+} ions, whereas at high temperatures it is due to polaron hopping [8]. The activation energies directly define the concentration of La^{3+} ions in parent $MnFe_2O_4$.

The frequency dependence of dielectric constant ε for synthesized compounds is presented in Fig. 4. The dielectric constant ε is seen to decrease with increasing

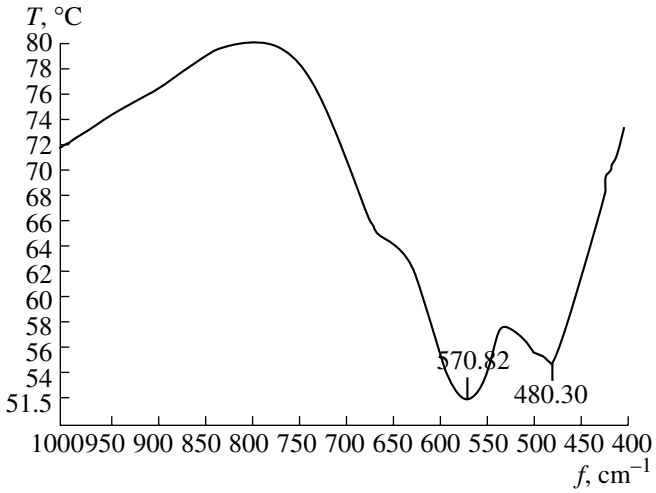

Fig. 2. FT-IR spectrum of $MnFe_2O_4$.

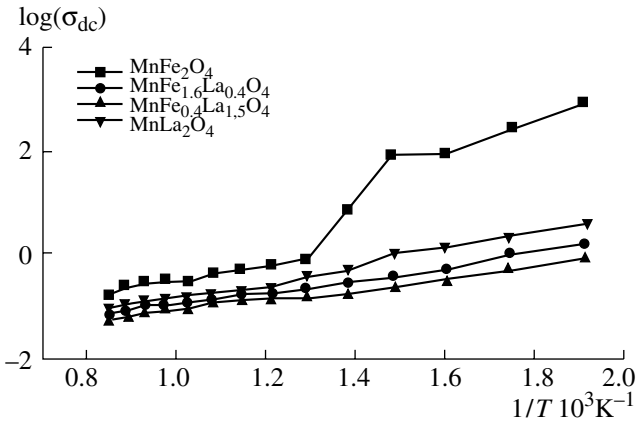

Fig. 3. Arrhenius plots in the $\log(\sigma_{dc}) - 1/T$ coordinates.

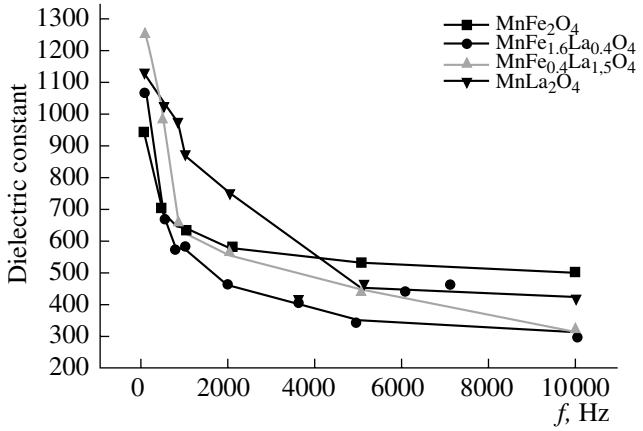

Fig. 4. Dielectric constant ε vs. applied frequency *f*.

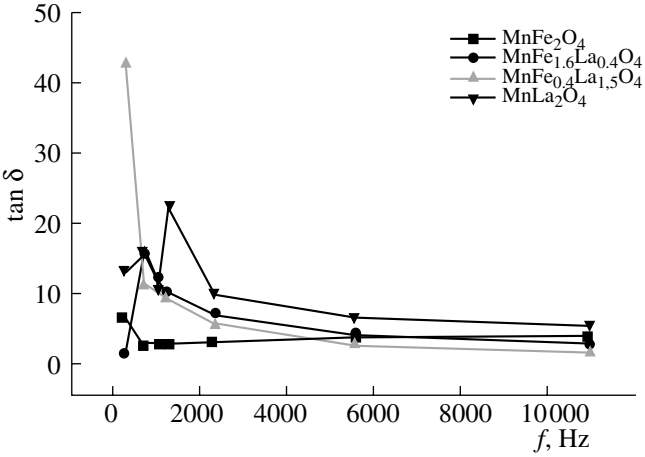

Fig. 5. Loss tangent tan ε vs. applied frequency *f*.

applied frequency *f*, which is a normal behavior of ferrite materials caused by the Maxwell–Wagner interfacial polarization. The polarization results in electron exchange between the ferrous and ferric ions, which gives rise to local displacements in the direction of applied external field. Similarly, the $Mn^{3+} \longleftrightarrow Mn^{2+} + e^+$ reaction gives the amount of holes in the octahedral sites that ensure local displacements in the direction opposite to the applied field. The above displacements are responsible for the polarizability and dielectric properties of the materials under consideration. As follows from Fig. 4, the lowest values of ε were exhibited by the $MnFe_{0.4}La_{1.6}O_4$ composition.

Figure 5 shows the loss tangent tan δ as a function of applied frequency *f*. For all of the samples studied, the values of $\tan\delta$ initially steeply increase/decrease and then level-off in the range of high *f*. A sharp drop in $\tan\delta$ is seen to happen around 0.5 KHz for $MnFe_2O_4$ and around 0.1 KHz for some La^{3+}-substituted ferrites. This difference can be associated with different type of localized electric charge in the compounds under study.

The frequency dependence of the ac electrical conductivity σ_{ac} for the synthesized samples is shown in Fig. 6. It is seen that σ_{ac} grows with increasing applied frequency *f*. This can be associated with an increase in the hopping frequency of the charge carriers between Fe^{2+} and Fe^{3+} in the octahedral sites by the mechanism suggested in [9].

CONCLUSIONS

The suggested combustion synthesis procedure was found to be a convenient tool for preparation of ferrite

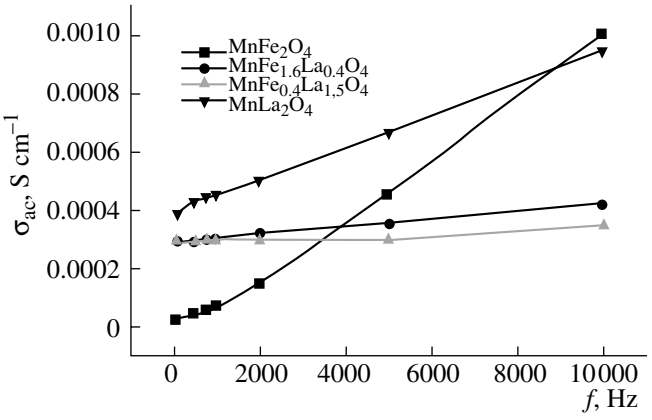

Fig. 6. The ac conductivity σ_{ac} as a function of applied frequency f.

materials. XRD data suggest that the synthesized compounds have a cubic structure. The lattice parameter was found to increase with increasing extent of La^{3+} substitution. FT-IR spectra show the characteristic features of spinel-type compounds. The dc electrical conductivity of the synthesized materials is typical of semiconductors. The maximum conductivity (18 S cm^{-1}) was attained in case of the $MnFe_{0.4}La_{1.6}O_4$ composition.

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