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Magneto-resistive coefficient enhancement observed around Verwey-like transition on spinel ferrites XFe_2O_4 (X = Mn, Zn)

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Manganese and Zinc ferrites were prepared by solid state reaction. The resulting powders were pressed into pellets and heat treated at 1100 °C. The samples were characterized by using X-ray diffraction, pure phases of zinc ferrite ($ZnFe_2O_4$) and manganese ferrite ($MnFe_2O_4$) were obtained. Scanning electron microscopy images showed a good contact between particles. A drop of electrical resistance was found in both samples, $MnFe_2O_4$ and $ZnFe_2O_4$, with values going from 2750 to 130 Ω and from 1100 to 55 Ω, respectively. Transition temperatures were determined to be $T_V = 225\,K$ for $MnFe_2O_4$ and $T_V = 130\,K$ for $ZnFe_2O_4$. Magnetoresistance measurements were carried out in the temperature range where R showed the transition, defined as the Verwey-like transition temperature range, ΔT_V. No magnetoresistive effect was observed out of it. The magnetoresistive coefficient (MRC) observed at ΔT_V reached its maximum values of 1.1% for $MnFe_2O_4$ and 6.68% for $ZnFe_2O_4$. The differences between MRC values are related to the divalent metal element used. Finally, the magnetoresistive response indicates that the electrical transition observed is strongly influencing the magnetoresistance; where the underlying responsible for this behavior could be a charge reordering occurring at the Verwey-like transition temperature. *© 2014 AIP Publishing LLC*. [http://dx.doi.org/10.1063/1.4857615]

I. INTRODUCTION

Spinel ferrites are an important class of materials. Their unique electronic, magnetic, and physical properties may be used in technological applications.[1–4] The spinel ferrite structure is described by the formula $(A)[B]_2O_4$; where oxygen atoms form a close packed lattice with transition metal ions located in the interstitial tetrahedral (A) sites and the octahedral (B) sites. The different ferrite systems can have normal or mixed spinel structure depending cation distribution. Numerous cations can be placed in the A and B sites to tune the magnetic and electronic properties of the material; also, are impacted by crystallite and particle size, crystal morphology, and the phase purity.[2–8] In these systems, the conduction phenomena have been described by the Verwey's hopping mechanism, where the mobility of electrons and holes affects the electrical conductivity. Here, the hopping probability depends on the separation of the ions and on the activation energy, which at the same time is dependent on temperature.[9–14] The magnetoresistive response has been found in some ferrite systems, which makes them more interesting for technological applications.[9,15] Therefore, in order to understand magnetoresistive phenomena, it is interesting to study the origin of the electrical resistance behavior during electrical transitions, and its effect on the magnetoresistance coefficient. In the present work, manganese and zinc ferrites were obtained by mechanical milling. Their electrical resistance and magnetoresistive coefficient as a function of temperature were analyzed. A Verwey-like transition was observed to affect the magnetoresistive properties.

II. EXPERIMENTAL METHODOLOGY

Zinc and manganese ferrites were prepared through solid state reaction technique. High energy ball milling (SPEX 8000M miller) was used to mix and mechanically activate the precursors, where Zinc Oxide (ZnO) and hematite (Fe_2O_3) were used for the $ZnFe_2O_4$ sample; and Manganese oxide (MnO) and hematite were used to form $MnFe_2O_4$. The precursor powders were stoichiometrically weighted and milled for 1 h. The as milled powders were pressed into cylindrical pellets. The pellets were heat treated at 1100 °C during 6 h for the manganese ferrite sample and 9 h for the zinc ferrite sample. The two samples were characterized by X-ray diffraction (XRD) using a PANalytical XPert Pro MPD diffractometer. XRD patterns were measured from 25° to 75° with a step of 0.016° and time per step of 30 s. The observation of morphology, particle sizes, and microstructure was conducted by scanning electron microscopy (SEM) in a field emission microscope JSM7000F. Finally, the electrical and magnetoresistive properties were measured in a VersaLab magnetometer. Resistance dependence with respect to temperature was studied in a temperature range from 300 to 50 K, using a

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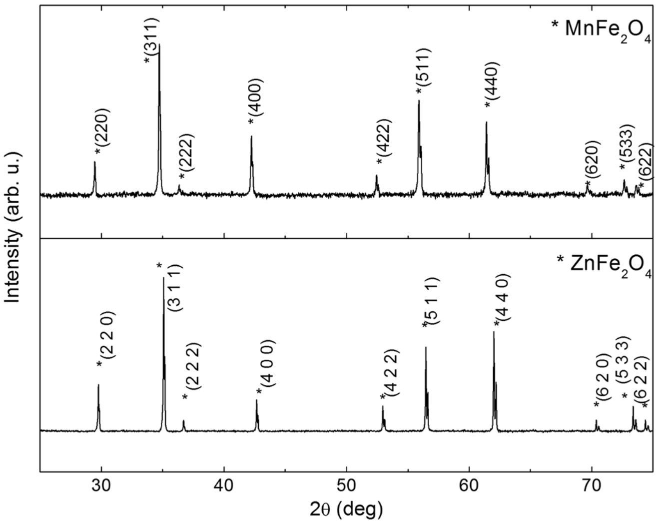

FIG. 1. XRD diffraction patterns for: (a) Manganese ferrite sample and (b) Zinc ferrite sample.

frequency of 57.9 Hz. The magnetoresistance analysis was carried out in different temperature ranges determined from the electrical behavior.

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns obtained for the manganese and zinc ferrite samples, in both cases the desired ferrite phase was found. XRD pattern of manganese ferrite sample, Figure 1(a), was indexed using the #PDF 01-073-1964 corresponding to the cubic spinel manganese ferrite phase. Figure 1(b) shows the diffractogram of the zinc ferrite sample. All peaks were identified with the #PDF 01-082-1042 of cubic spinel zinc ferrite pure phase. No secondary phase peaks were observed.

Figure 2 exhibits two characteristic SEM micrographs of (a) manganese ferrite and (b) zinc ferrite samples. Both samples showed a laminar growth. The manganese ferrite has well defined sharp grain boundaries; while for zinc ferrite sample the grain boundaries are smooth. A good contact between particles is observed in both samples with an evidence of necks and big grains that correspond to a sintering process. Average particle sizes, $\langle D\rangle_{part}$, calculated for each sample were 2.8 μm for manganese sample and 1 μm for zinc ferrite sample. Particle size distributions are wide for both samples and can be observed at the inset graphs in Figure 2.

Figure 3 shows the R(T) curve obtained for (a) $MnFe_2O_4$ and (b) $ZnFe_2O_4$ samples. Both samples showed a drop in the resistance while lowering the temperature. For manganese ferrite this drop was from 2750 to 130 Ω, and for zinc ferrite the drop was from 1100 to 55 Ω. This electrical behavior was attributed to a Verwey-like transition, defined as the metal-insulator transition observed by Verwey in magnetite at 120 K.[11,14] Since the mobility of charge carriers is temperature dependent, an increase in the mobility might have caused a reduction in the electrical resistance due to a change in activation energy.[10] The exact explanation of the drop on the resistance is still unknown; however, due to the similarities on the spinel structure and the electrical response of ferrites, the Verwey hopping mechanism is proposed to describe the observed transition in the present ferrite system. The transition temperatures, T_V, were calculated from the derivative curve obtaining values of 225 K for $MnFe_2O_4$ and 130 K for $ZnFe_2O_4$. These temperature values could be attributed to the different cation sizes and distributions in this ferrite system.[12,16]

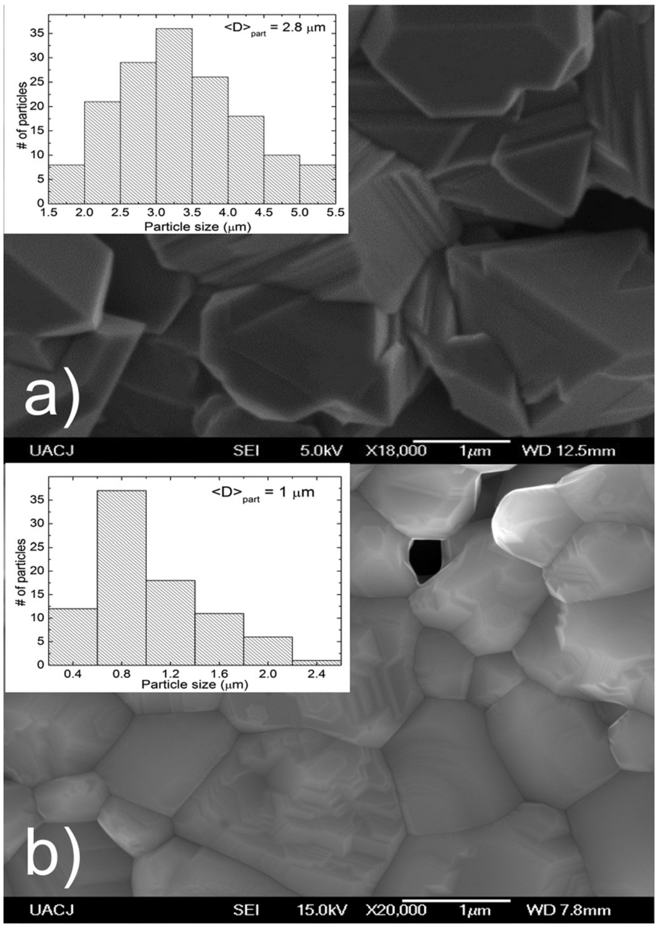

FIG. 2. Characteristic SEM images of: (a) manganese ferrite sample and (b) zinc ferrite sample. At the insets the particle size distribution calculated for each sample.

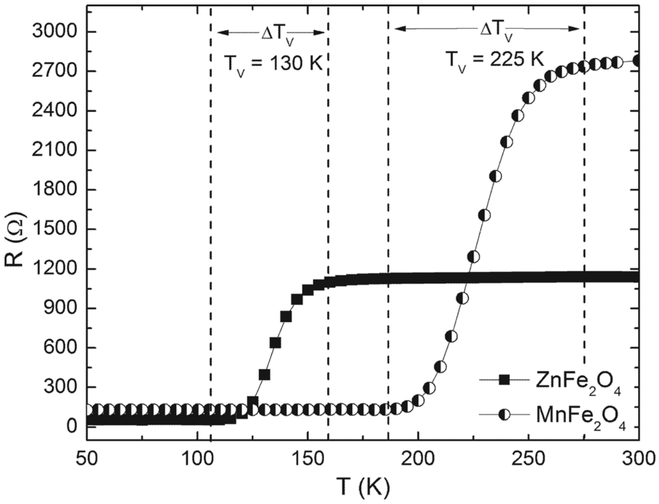

FIG. 3. Resistance curves against temperature. Verwey transition temperature ranges (ΔT_V) are indicated.

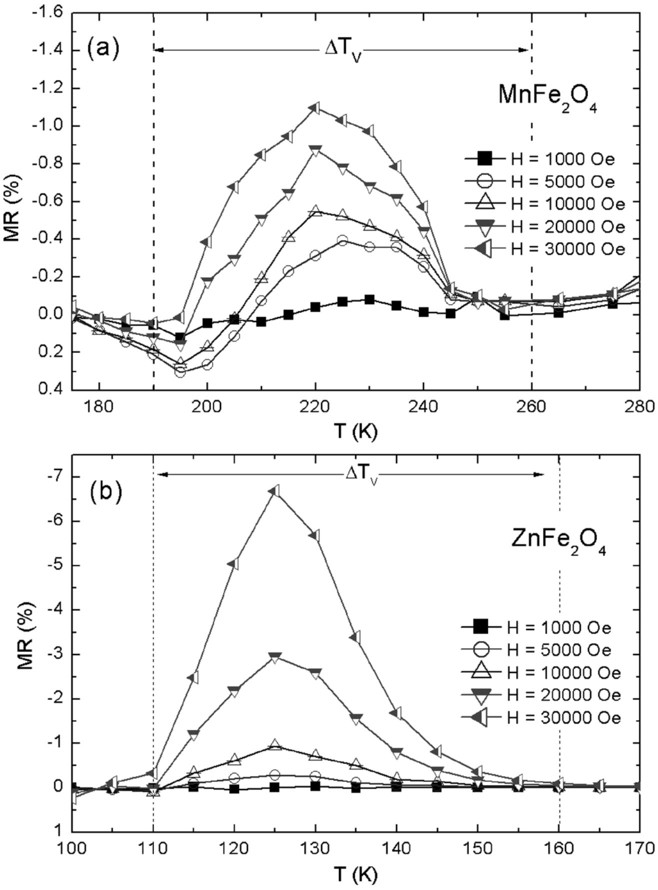

FIG. 4. Magnetoresistance coefficients observed at different magnetic fields in the Verwey transition temperature range for samples: (a) $MnFe_2O_4$ and (b) $ZnFe_2O_4$.

Figure 4 shows the results of the magnetoresistive coefficient (MRC) as a function of temperature, at different magnetic fields, for (a) manganese and (b) zinc ferrites. It can be observed that during the Verwey-like transition temperature range, defined as ΔT_V, magnetoresistive effect appears; while for temperatures out of ΔT_V, magnetoresistive effect is despicable. The maximum MRC observed in manganese ferrite was 1.1% at a temperature of 220 K near transition temperature; whereas, for zinc ferrite, the maximum MRC was 6.67% at 125 K. The differences between the T_V determined from R(T) curves and the temperature, where maximum magnetoresistance occurs, are attributed to the particle size distribution of the ferrite samples. It could be explained as follows: since the conduction phenomena are dependent on charge carriers, and at the same time it is dependent on the crystalline structure and particle size; the magnetoresistance phenomenon is affected not only by the transition temperature but also by the particle size distribution. The magnetoresistive behavior indicates that the electrical transition observed in the R(T) curves is strongly influencing the magnetoresistance of the present ferrite system. A possible explanation can be suggested in the basis of Verwey transition, in which the mobility of charge carriers could drive to a crystalline structure change. Therefore, when a magnetic field is applied the conduction could be facilitated through a spin driven conduction, giving place to the observed magnetoresistive effect on these ferrites.[12–14,17,18] Even though a good understanding on the Verwey-like transition is not clear yet, the fact that the conduction phenomena are affecting directly in the MRC could lead to a better understanding of this electrical transitions and its origin.

IV. CONCLUSIONS

Manganese and Zinc ferrites were prepared by solid state reaction. Pure phases of zinc ferrite and manganese ferrite were achieved. The electrical resistance plots showed a drop in the resistance attributed to a Verwey-like transition. Verwey transition temperatures values were determined on $T_V = 130$ K for $ZnFe_2O_4$ and $T_V = 225$ K for $MnFe_2O_4$. The magnetoresistive coefficient was observed in the temperature range of Verwey transition, ΔT_V. It was observed that MRC is almost 0% in temperatures out of ΔT_V; however, as the temperature approximates to the T_V value, the MRC increases reaching to its maximum value when temperature is almost. Maximum MRC calculated were 6.68% for $ZnFe_2O_4$ and 1.1% for $MnFe_2O_4$. The magnetoresistance appearance was explained in the basis on the Verwey-like transition observed at the R(T) plots.

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