Structure, Electrical and Dielectric Properties of Strontium Europium Ferrimanganites

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Abstract: The present work is devoted to the microstructure, electrical properties and Raman scattering study of $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ where (x= 0.1 and 0.5). These compounds were prepared from pure oxides using standard solid state reaction. The final sintering temperature was 1350°C for 72 h. The synthesized semiconductor composites were studied in details in terms of their morphological and structural properties. It crystallizes with orthorhombic system of space group P_{bnm}. XRD test showed that $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ where (x= 0.1 and 0.5) that this composite is stable with time. The energy dispersive spectroscopy EDS reveals that the synthesized composites are in proper stiochiometry of the proposed structure. The increase in the grain size with the increase of iron concentration is observed. The DC resistivity dependence on temperature measurements for $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ show that these compounds have semiconductor behavior with activation energy 0.152 eV for Sample of x=0.1 increase to the value 0.535 eV for the sample x=0.5. The difference in ac resistance between iron concentration; x=0.1 and x=0.5 is very big at low frequency and is very small at high frequency. In the frequency range from 75kHz up to 3MHz dielectric of $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ shows decrease in the dielectric constant with increasing of frequency of the x=0.1 sample and at frequency 150kHz change in behavior occurred where slight increase in dielectric with increase in frequency. The same behavior observed for the sample x=0.5 but the change point appears at frequency 250kHz.
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1. Introduction

In the recent years, a lot of interest has been devoted to research on rare earth manganese perovskites due to their potential and technological applications and the fascinating physical phenomena they exhibit, such as colossal magnetoristance (CMR), metal-insulator (MI) and charge ordering (CO) [(1-3)]. Since 1950, the striking correlation between unusual electrical and magnetic properties for such compounds is very interesting subject [(4, 5)]. $R_yA_{1-y}MnO_3$ is one of the most extensively studied system, where R is a rare earth element, A is a divalent element like Ca, Sr, Ba, … They have an orthorhombic distortion perovskite-like structure [(6)] where R occupies site in which it is surrounded by distorted 12 oxygen atoms polyhedra while the oxygen octahedra around the Mn ones are less distorted The important correlation between crystal structure of materials and their transport properties reported in ref. [(7)] where the tilt in octahedra plays an important role in.defining the magnetic and electric exchange interaction between transition metal elements *eg* and Oxygen *2p* orbitals of such compounds. On other words, the distortions occurred in lattice play very important role in defining electrical and magnetic transport in these materials. It should be only caused by the average ionic radius of the A-site element $\langle r_A \rangle$, which is governed by the tolerance factor t. This tolerance factor is defined as [(8)];

$$t = (\langle r_A \rangle + \langle r_O \rangle)/\sqrt{2}(\langle r_B \rangle + \langle r_O \rangle)$$

where $\langle r_A \rangle$ is the average ionic radius of A-site ions (Eu^{3+} and Sr^{2+}) and ($\langle r_B \rangle$ is the average ionic radius of the B-site ions (Mn and Fe) in our studied samples.

As reported by Li et. al., [(8)], when t is close to 1, a cubic perovskite structure is expected to form. For $(Eu_{1-x}Pr_x)_{0.6}Sr_{0.4}MnO_3$ samples, as $\langle r_A \rangle$ increases, so does t. This may interpret the lattice structure structure becomes more ordered and accompanied by the change in the orthorhombic structure types from the O′-type and O″-type structure, to an O*-type orthorhombic structure. The change in orthorhombic structure types at room temperature attributed to the difference in the rare earth ionic radius as mentioned By Li *et al*[(8)].

Electrical conductivity of $Nd_xSr_{1-x}CoO_3$ was investigated by Vargas *et al.,* [(9)] the small polaron hopping conductivity model was described and there was increase in the conductivity due to regular increments of Sr content for all compositions. The reduction of the working temperature of the solid oxide fuel cells (SOFC)

down to the 800-850ºC range was investigated to develop new electrodes with the adequate ionic and electronic conductivity at those temperatures [10]. It was stabilized the cubic phase of the $SrCoO_3$-δ perovskite through Sb doping in $SrCo_{1-x}Sb_xO_{3-d}$ [6] and its electrical properties was studied. According to Abdel-Latif *et al.* [5] who reported that $Nd_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$ represents semiconductor behavior and its activation energy is directly proportional to the unit cell volume where unit cell increase with iron concentration increase. According to Abdel-Latif *et al.* and Dunaevsky *et al*[11, 12] in spite of both $Sm_{0.6}Sr_{0.4}MnO_3$ samples have the same structure (lattice constant are almost the same) and are prepared using the same method (solid state reaction) they have different MR values which interpret by the difference in distortion.

Therefore**,** the **s**tudy of microstructure and crystal structure characterization and its relation with the substitution of manganese by iron is represented in the present paper. As well as studying the dc and ac electrical properties and Raman spectroscopy was performed.

2. Experimental Details

$Eu_{0.65}$ $Sr_{0.35}$ $Mn_{1-x}Fe_xO_3$ (x = 0.1 and 0.5) were prepared from the initial pure oxides (Eu_2O_3, Fe_2O_3, Mn_2O_3 and SrO) using the solid state reaction method. These pure oxides were well mixed with appropriate ratios to be milled together using agate mortar then pressed in disk form under a pressure = 15 ton/cm^2. The pressed disks were fired at 1200°C for 12 h in air. The pre-sintered samples were ground again and pressed under the same pressure in the form of disk with 12 mm diameter. All samples were fired again at 1350°C for 72 h with an intermediate grinding to ensure homogenization; this heat treatment was followed by natural furnace cooling.

The elemental analysis using the energy dispersive X-ray spectroscopy **(**EDXS spectra), and micrograph measurements were carried out using Field Emission Scanning Electron Microscope FE-SEM – JEOL (JSM-5600) with acceleration voltage 15kV and magnification of X-43000.

The XRD measurements were performed using a PANalytical X'pertPro MPR diffractometer with Cu radiation.

The DC resistivity –temperature dependence measurements were carried out using four points probe technique (Scientific Equipment & Services) in the temperature range from room temperature to 573 K.

The AC resistance, capacitance and dielectric measurements were carried out using LCR meter (HP 4284A) in room temperature.

3. Results and Discussion

The phase formation of the synthesized samples is tested using X-ray diffraction in 2005 and the results of the refinement parameters for these samples are reported By Farag *et al.* [13]. XRD for the same samples are measured after 6 years and presented in this work, see Fig.1. It is quite clear that all reflections are corresponding to the orthorhombic crystal system of space group *Pnma* (No 62). The lattice parameters which were deduced from XRD patterns represented in fig. 1 were found to be the same values of those measured 6 yeas before and reported By Farag *et al.* [13] .

Comparing lattice parameters of $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ where (x= 0.1 and 0.5) with those measured 6 years ago for the same concentration it is clear that no change occurred in the crystal structure of $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ with time that is good indication for the stability of this composition.

The elemental analysis using EDXS was carried out for both samples. The following standards; SiO_2, Mn, Fe, SrF and EuF were used for identifying Oxygen O, manganese Mn, Iron Fe, Strontium Sr and Europium Eu elements respectively that constitute $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$. The obtained peaks correspond to Oxygen, Manganese, Iron, Strontium and Europium which forms the $Eu_{0.65}$ $Sr_{0.35}$ $Mn_{1-x}Fe_xO_3$.

From EDXS spectra of $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$, one can note that there are no impurities in the content of the proposed compounds which is good indication to the quality of synthesis. The concentration of each element in the compound are in good agreement with the theoretically calculated, see table 1. As it is quite clear that, the experimentally observed percentages of elements (which constitute the proposed composites) are in good agreement with those calculated. The elemental analysis reveals that the synthesized composites of the proposed structure are in proper stoichiometry and this is in a good agreement with the crystal structure analysis using X-ray diffraction which reported separately [13].

The microstructure graphs $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$ are taken at 15KeV and magnification x43000 (Fig. 2). From Figure (2), it is clear that the grain size of in the composite where x=0.1 is on the range of 2.5 – 3.5 μm. One can say that the homogeneity in the size of grains is not completely represented. Looking at

the microstructure of composite where x=0.5 one can note that the lower grain size is quite clear compared with the grain size in x=0.1. The grain size in the case of x=0.5 in the range 0.5 – 1 μm. Recently reported by Rößler *et al.,* [15] that the morphology of thin films has a strong influence on the local conductivities in manganite thin films. The magnetic properties of manganites also depend on the morphology of these manganites. It was reported by Marttinez *et al.,* [16], that the magneto resistance and the magnetization of ceramic $La_{2/3}A_{1/3}MnO_3$ (A = Sr, Ca) oxides have been studied as a function of the grain size. It was found that [17] these ceramics become magnetically harder when reducing the particle size exhibiting a large magnetic anisotropy that increases when reducing the grain size.

The DC resistivity – temperature dependence measurements of $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ (x=0.1 and 0.5) after sintering at 1350°C for 72 hours are shown in Fig. (4) and Fig (5). The temperature dependence of the resistivity curve of both samples shows the semiconductor behavior where the resistivity of $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ decreases with increasing temperature.

The relation between resistivity and temperature expressed in the exponential dependence and the well known Arrhenius equation gives the best fitting of the experimental measurements [19].

$$\rho = \rho_o e^{\frac{-E}{kT}}$$

where ρ_0 is the resistivity at room temperature, E is activation energy, k is Boltzmann constant and T is absolute temperature according to this formula one can calculate the activation energy which has the value of 0.152 eV and 0.535 eV for x=0.1 and x=0.5, respectively. From the linear dependence of the M – O bond length and the volume of unit cell of $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ on the iron concentration reported by Ahmed Farag et al [13], one can correlate the increase of increase in the bond length and activation energy of $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ with the increasing iron concentration. This increase in bond length may explain the increase in the resistivity that is in good agreement with the case of the $Nd_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ in which the increase in the iron content related to the increase in resistivity as reported by Abdel-Latif *et al.* [5].

The AC resistance, capacitance and dielectric measurements are shown in Fig.5. A decrease in the AC resistance is observed in both concentration of $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ with increasing frequency. The difference in ac resistance between iron concentration; x=0.1 and x=0.5 is very big at low frequency and is very small at high frequency. The capacitance decreases with increasing frequency in x=0.1 while for x=0.5 it decrease with increasing frequency and at frequency near 300 kHz behavior changed and it start increasing with increase in frequency. In the frequency range from 75kHz up to 3MHz dielectric of $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ shows decrease in the dielectric constant with increasing of frequency of the x=0.1 sample and at frequency 150kHz change in behavior occurred where slight increase in dielectric with increase in frequency. The same behavior observed for the sample x=0.5 but the change point appears at frequency 250kHz. The dielectric constant of sample with lower iron concentration is smaller than that of higher iron concentration.

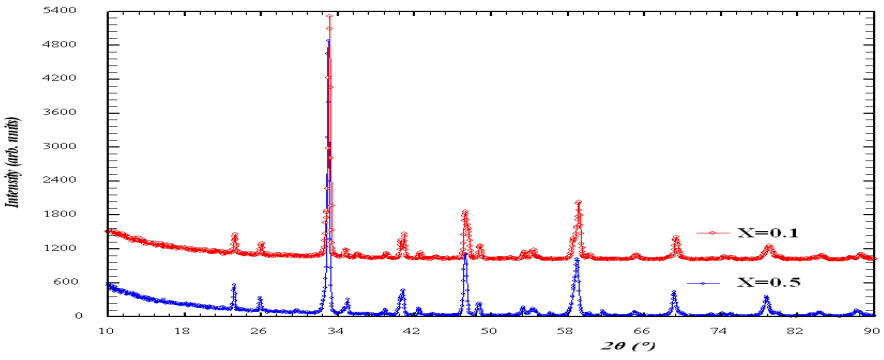
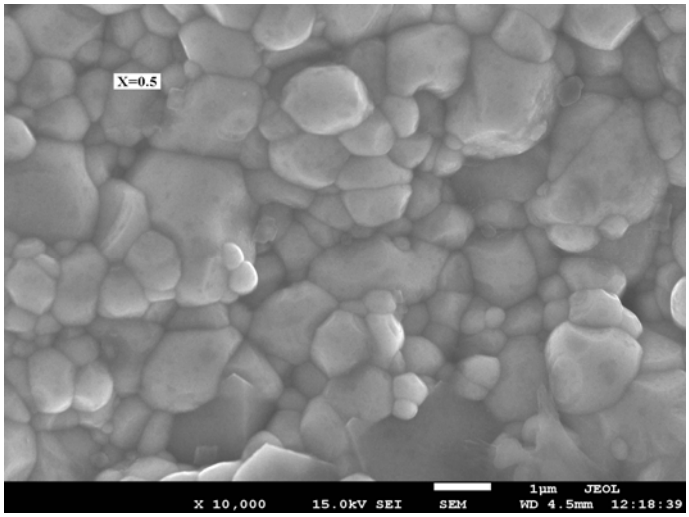
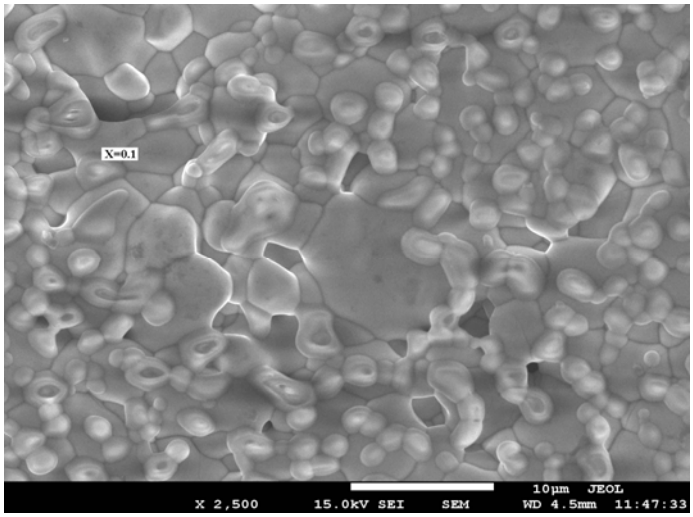


Fig. 1 XRD patterns of $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$ (X= 0.1 and 0.5).



X=0.5



X=0.1

Fig. (2) Micrographs of $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$ (X= 0.1 and 0.5) measured at 15 kV.

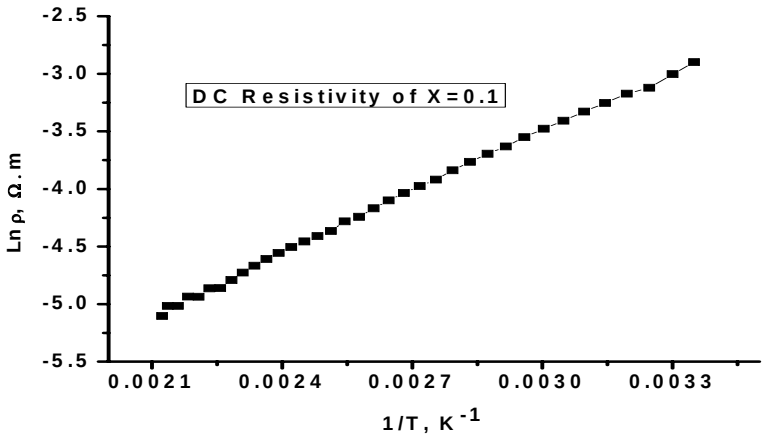


Fig. (3) DC resistivity – temperature dependence of $Eu_{0.65}Sr_{0.35}Mn_{0.9}Fe_{0.1}O_3$

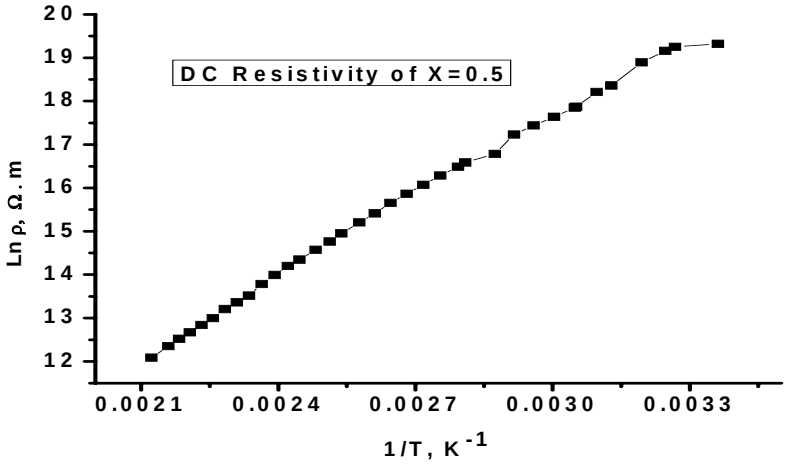


Fig. (4) DC resistivity – temperature dependence of $Eu_{0.65}Sr_{0.35}$ $Fe_{0.5}Mn_{0.5}O_3$.

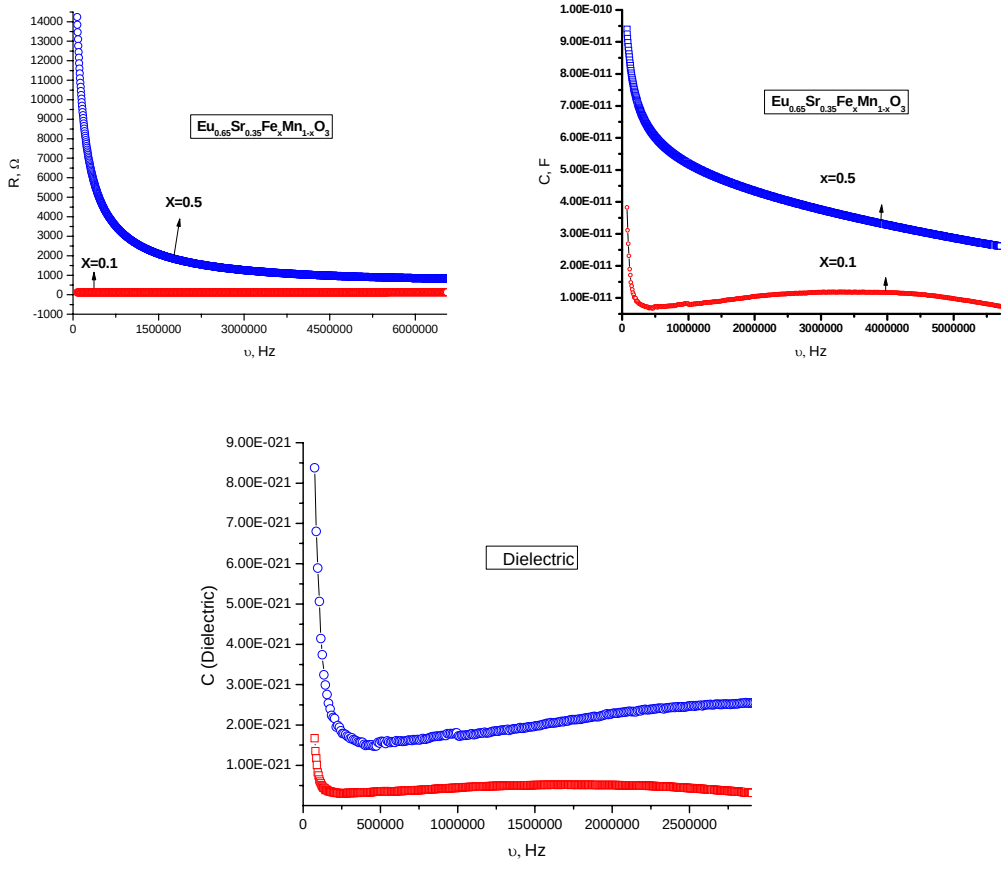


Fig. (5) AC resistance, capacitance and dielectric measurements of $Eu_{0.65}Sr_{0.35}$ $Fe_{0.5}Mn_{0.5}O_3$.

Table 1. Elements identifications of $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$

X	0.1		0.5	
Element	**Exp.Weight %**	**Cal. Weight %**	**Exp.Weight %**	**Cal. Weight %**
O	18.67	20.65	28.49	20.62
Mn	21.05	21.27	10.41	11.80
Fe	3.56	2.40	11.26	11.99
Sr	7.05	13.19	11.38	13.17
Eu	49.67	42.49	38.46	42.43
Totals	100.0	100.0	100.0	100.0

Conclusions

The DC resistivity - temperature dependence measurements for $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ represent the semiconductor behavior with activation energy 0.152 eV and 0.535 eV values for the samples of x-0.1 and x=0.5 respectively.

The microstructure study showed that the grain size decreases with increasing the iron concentration.

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