Study on structure, electrical and dielectric properties of Eu$_{0.65}$Sr$_{0.35}$Fe$_{0.3}$Mn$_{0.7}$O$_3$

I. A. Abdel-Latif
Physics Department, College of Science & Arts, Najran University,
P. O. 1988 Najran, Kingdom of Saudi Arabia
Reactor Physics Department, NRC, Atomic Energy Authority,
Abou Zabaal P. O. 13759, Cairo, Egypt
E-mail: ihab_abdellatif@yahoo.co.uk

Abstract. Polycrystalline Eu$_{0.65}$Sr$_{0.35}$Fe$_{0.3}$Mn$_{0.7}$O$_3$ was synthesized using a standard solid state reaction technique. The preliminary microstructure of this compound at room temperature was studied using a field emission scanning electron microscope (FESEM), and the crystal structure was investigated using X-ray diffraction (XRD). The considered compound was found to crystallize in a single-phase orthorhombic structure in the $Pbnm$ space group (62). The Raman spectrum shows three Raman-active vibrational modes at approximately 208, 476 and 616 cm$^{-1}$. The temperature variation of the resistivity shows that these compounds have semiconductor behaviour with an activation energy 0.498 eV. The frequency dependence of the dielectric constant in these materials indicates that space charge polarization contributes significantly to their observed dielectric parameters.

1. Introduction
Over the last few decades, the ABO$_3$ perovskite structure has attracted scientific interest due to its remarkable properties. The technologically useful properties exhibited by these perovskite-type oxide materials are electrical, magnetic, dielectric, and optical. Among these materials, the doped rare-earth manganites R$_x$A$_{1-x}$MnO$_3$ have been extensively investigated by several researchers [1-4] because of their scientific significance and potential applications [5]. In particular, these systems exhibit the novel phenomena of colossal magnetoresistance (CMR), metal-insulation (MI) and charge ordering (CO), in manganites [6-8]. The underlying physics of those phenomena has been interpreted in terms of the double exchange (DE) model, in which a strong exchange interaction occurs between Mn$^{3+}$ and Mn$^{4+}$ ions through intervening filled oxygen 2p states [9], the Jahn-Teller (JT) polaron, and a tolerance factor [10]. Knowledge of the crystal structure and the chemical bonding of these compounds is of a great importance to the understanding of the peculiar electro transport and magneto transport properties in these perovskites. It is known that the $A$-site substitution primarily changes the carrier density and strongly affects the Mn$^{3+}$-O-Mn$^{4+}$ angle (lattice distortion), thus transforming the parent compound RMnO from an insulating antiferromagnet into a metallic ferromagnet [11]. Alternatively, the $B$-site substitution directly modifies the crucial Mn$^{3+}$-O-Mn$^{4+}$ network. The important correlation between the crystal structure of the materials and their transport properties are reported in [12-14], where the tilt in the octahedra plays an important role in defining the magnetic and electric exchange interaction between transition metal element $e_g$ orbital and oxygen 2$p$ orbital. The composition and microstructure of ABO$_3$ may be modified by doping in the A site or the B site or by simultaneous
doping to tailor the properties to specific applications [15-20]. To describe the ion match between A and B ions in this type of compound, a geometrical quantity, the tolerance factor $t$, is usually introduced; $t$ is defined as [17]:

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

where $\langle r_A \rangle$ is the average ionic radius of the 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. In this case, the average ionic radius of the A-site is fixed. Thus, the lattice distortion observed is caused by the partial replacement of Mn by Fe. Therefore, the structural studies of manganites doped by Fe with systematic compositional variation can be advantageous for gaining important insight into the structure–property relationships for these compounds. Eu$_{0.65}$Sr$_{0.35}$Fe$_x$Mn$_{1-x}$O$_3$ (x = 0.1 and x = 0.5 compounds were studied in ref. [21], so that it is very important to complete the series and see what the difference and the effect of iron substitution. The valence of manganese in Eu$_{0.65}$Sr$_{0.35}$Mn$_{1-x}$Fe$_x$O$_3$ is $(0.35\text{Mn}^{3+} + 0.15\text{Mn}^{4+} + 0.2\text{Mn}^{3+})$ where the double exchange phenomenon is complete. The valence of manganese is $(0.35\text{Mn}^{3+} + 0.15\text{Mn}^{4+})$ in Eu$_{0.65}$Sr$_{0.35}$Mn$_{0.5}$Fe$_{0.5}$O$_3$, whereas, double exchange is not complete. As it is clear that the valence of manganese in Eu$_{0.65}$Sr$_{0.35}$Fe$_{0.3}$Mn$_{0.7}$O$_3$ is the critical case.

The purpose of the present work is to study the structural, electrical and dielectric properties of iron-doped europium ferrimanganites with a critical concentration of iron of $x=0.3$.

2. Experimental details

The sample synthesis and preparation are performed using a conventional solid-state reaction. The proper stoichiometric amounts of pure oxides were carefully mixed, and then the mixed powder was pressed at 2 tons. The pellet was fired at 1100°C for 12 h in air. The pre-sintered sample was ground again into a fine powder and then pressed and fired at 1200°C for 12 h. After repeating the grinding and pressing of the powder, it was finally fired at 1350°C for 72 h, followed by natural furnace cooling. The phase purity and crystallographic information of the synthesized samples were tested using powder X-ray diffraction (XRD). The XRD analysis was performed using a PANalyticalX’ PertPRO diffractometer at room temperature with Cu-Kα radiation ($\lambda=1.5406$ Å). Micro-structural observations and chemical analysis were performed on the samples using a field emission scanning electron microscope (FESEM) (JEOL JSM-7600F) combined with energy dispersive spectroscopy (EDS). The Raman spectra were obtained using a (Perkin Elmer) Raman spectrometer in the 3000-600 cm$^{-1}$ region at 4 cm$^{-1}$ resolution in a continuously purged sample compartment. The DC resistivity–temperature dependence measurements were performed using the four-point probe technique (Scientific Equipment & Services) in the temperature range from room temperature to 573 K. The dielectric characteristics at room temperature were determined using an inductance–capacitance–resistance (LCR) meter (HP4284A).

3. Results and discussions

The surface morphology and microstructure analysis of the samples have been investigated using FESEM and EDS analysis. Figure 1 shows the morphology and the crystalline size of the synthesized sample. Upon examining the morphology of the Eu$_{0.65}$Sr$_{0.35}$Mn$_{1-x}$Fe$_x$O$_3$ samples ($X=0.1$, 0.3 and 0.5), we find that there is a fairly uniform grain size distribution throughout the surface that becomes non-uniform as the iron concentration increases. Our morphological investigation reveals the absence of high-density cracks. This result is an indication that we have a good-quality material with a minimum number of defects. These micrographs show that doping with Fe$^{3+}$ strongly reduces the grain size, which decreases from 2.5-3.5 μm for $x = 0.1$ to 0.5-1μm for $x = 0.5$, i.e., substitution of Fe for Mn leads to a reduction in the grain size. Accordingly [22], the specimens become magnetically harder.
Figure 1. (a) EDS spectrum of Eu$_{0.65}$Sr$_{0.35}$Mn$_{0.7}$Fe$_{0.3}$O$_3$ and (b) SEM micrograph of Eu$_{0.65}$Sr$_{0.35}$Mn$_{1-x}$Fe$_x$O$_3$ samples (X=0.1, 0.3 and 0.5) when reducing the particle size and exhibit a large magnetic anisotropy upon reducing the grain size. Micro-qualitative analysis using EDS was performed for our sample; the results indicate that all of the elements of our compound are in the proper ratio. From the EDS result of Eu$_{0.65}$Sr$_{0.35}$Mn$_{1-x}$Fe$_x$O$_3$, no impurities were found in the content of the proposed compounds, indicating the quality of the synthesis. The experimentally observed percentages of elements (which constitute the proposed composites) are clearly in good agreement with those predicted theoretically.

X-ray powder diffraction investigations at room temperature indicated that the samples were single phase with no detectable secondary phases, see Figure 2. XRD data for the system Eu$_{0.65}$Sr$_{0.35}$Mn$_{0.7}$Fe$_{0.3}$O$_3$ are given in Table 1. All of the reflection peaks in the measured XRD pattern were indexed according to the orthorhombic symmetry of the space group $Pbnm$ (No. 62). However, a minor shift is observed in the peak positions, indicating a small change in the lattice parameters. The orthorhombic unit cell volume increases slightly due to differences in ionic radii of Mn$^{3+}$ and Fe$^{3+}$ ions [23]. Due to the increase in the iron concentration, both the full-width at half
maximum (FWHM) (broadness) and the intensities of the peaks increased. The broadness of the peaks indicates either particles of very small crystalline size or particles that are semicrystalline in nature [24]. The maximum reflection intensity corresponds to the 112 plane; see Figure 2. The lattice parameters resulting from fitting of the experimental XRD patterns using the Fullprof program [25] are listed in Table 1. The simple formula for the [b] and [c] tilt are shown in ref. [14]. The first-order approximation of the [b] and [c] tilt are given as following; \( [b] \text{tilt} = (180 - \alpha)/2 \) and \( [c] \text{tilt} = (180 - \beta)/2 \) where \( \alpha \) and \( \beta \) are Mn-O1-Mn and Mn-O2-Mn angles, respectively. From the results of XRD refinement, we found that the value of Mn-O1-Mn and Mn-O2-Mn angles equal 168.40° and 153.87°, respectively. So the resulting tilt angles were calculated for Eu\(_{0.65}\)Sr\(_{0.35}\)Fe\(_{0.3}\)Mn\(_{0.7}\)O\(_3\) to be; \([b] \text{tilt} = 5.8°\) and \([c] \text{tilt} = 13.1°\). Comparing with the tilt angles in Sm\(_{0.6}\)Sr\(_{0.4}\)MnO\(_3\) our sample has more distortion than it. looking at the lattice parameters of Eu\(_{0.65}\)Sr\(_{0.35}\)Fe\(_{x}\)Mn\(_{1-x}\)O\(_3\) (where \( x = 0.1, 0.3 \) and 0.5) previously reported for the same concentration[26], it is clear that no change occurred in the crystal structure of the present system over time, indicating the stability of this composition. The XRD results are consistent with the FESEM results.

The scattering density inside the unit cell of a crystal, regardless of the symmetry, is calculated using Fourier as a subprogram in Full Prof. A Fast Fourier Transform (FFT) is applied as a subroutine to accelerate the calculation of the following expression:

\[
\rho(r) = \frac{1}{V} \sum_H \mathcal{F}(H) \exp\{-2\pi i (H \cdot r)\}
\]

Where \( V \) is the volume of the unit cell, \( H \) is the reciprocal lattice vector, \( r \) is the vector position inside the unit cell, and \( \mathcal{F}(H) \) are complex Fourier coefficients used to perform different types of Fourier
syntheses. The units of $\rho \ (r)$ are those of $F \ (H)$ divided by those of $V$. The density of electrons inside the unit cell is calculated as shown in Figure 3.

Raman spectroscopy is a powerful technique for studying and characterizing the lattice-vibrational properties. Raman spectroscopy is not only used to probe the spin–phonon interaction but also accounts for the electron–phonon interaction and is effective in manganites. Thus, the symmetry information regarding phonon, electron, and spin excitations can be simultaneously explored using this technique. The optical mode frequencies in the vibrational spectra of manganites are shown in the literature, either by theoretical or experimental studies, and are interpreted on the basis of lattice distortions.

**Table 1.** Cell parameters and atomic parameters

| Atom | Ox. | S.O.F. | x/a | y/b | z/c | V (Å³) | a/b | b/c= | c/a |
|------|-----|--------|-----|-----|-----|--------|-----|------|-----|
| O2   | -2  | 1      | -0.28229 | 0.27634 | 0.05029 | 0.0013 |
| O1   | -2  | 1      | 0.02896  | 0.47896 | 0.25000 | 0.0132 |
| Sr   | +2  | 0.35   | -0.00481 | 0.0372(5) | 0.25000 | 0.0086 |
| Eu   | +3  | 0.65   | -0.00481 | 0.0372(5) | 0.25000 | 0.0086 |
| Mn   | +3  | 0.7    | 0.50000 | 0.00000 | 0.00000 | 0.011 |
| Fe   | +3  | 0.3    | 0.50000 | 0.00000 | 0.00000 | 0.011 |

It is well known that the Raman-active mode of lattice vibrations is absent in the ideal cubic perovskite, and the Raman-active modes of the orthorhombic structure are as follows: $A_g+B_{1g}$ symmetric and $2B_{2g}+2B_{3g}$ antisymmetric stretching modes; $A_g+2B_{1g}+B_{3g}$ bending modes and $2A_g+2B_{2g}+B_{1g}+B_{3g}$ rotation and tilt modes of the octahedral structure; and $3A_g+B_{2g}+3B_{1g}+B_{3g}$ modes related to the rare earth movement. Therefore, the vibrational bands reported in [26-31] for various
families of the manganite compounds were taken as a reference for the discussion of the present observed spectrum. Thus, we can use Raman spectroscopy to study the lattice distortions in Eu$_{0.65}$Sr$_{0.35}$Fe$_{0.3}$Mn$_{0.7}$O$_3$ (Figure 4) and compare the data with the data induced by the doping effect. The main features observed in the spectrum at room temperature are the three bands centered at approximately 210, 490 and 610 cm$^{-1}$. The assignment of these modes is based on the lattice dynamic calculation [28] and is similar to the results of Choi et al. [31]. In our case, the spectrum at room temperature three bands centered at approximately 208, 476 and 616 cm$^{-1}$. The 208 cm$^{-1}$ (low-frequency mode) band is attributed to the A$_{1g}$ mode, which is the in-phase rotation of the oxygen cage about the y-axis to the adjacent MnO$_6$octahedra. The mode near 476 cm$^{-1}$ corresponds to the out-of-phase bending (asymmetric stretching) mode (B$_{2g}(3)$), which is associated with the JT distortion and is sensitive to a change in the Mn-O-Mn bond angle. The mode observed at 616 cm$^{-1}$ is due to symmetric stretching of the basal oxygen ion (B$_{2g}$ (1)). By comparing these results with those published by I A Abdel-Latif and S A Saleh [21], it is clear that no major change in the shape and position of the characteristic vibration bands with the increase in Fe content has been observed. With an increase in the iron content in Eu$_{0.65}$Sr$_{0.35}$Mn$_{0.5}$Fe$_{0.5}$O$_3$, the A$_{1g}$ mode is slightly shifted toward higher frequency (216 cm$^{-1}$). The bending mode (B$_{2g}(3)$) is observed to be shifted to lower frequency (476 cm$^{-1}$). Because the B$_{2g}(3)$ modes are sensitive to the change in the Mn-O-Mn bond angle, the variation of this mode directly reflects the change of the bond angle. The peak for the stretching mode (B$_{2g}$ (1)) gradually becomes stronger and moves slightly to higher frequency as a result of the increasing in Fe$^{3+}$ concentration. This stretching mode is sensitive to a change in the bond length of the Mn-O bond. From the lattice dynamic calculations, the most intense modes, that is, those at 210 - 216, 488 - 491, and 610 - 632 cm$^{-1}$, are associated with rotational-, bending-, and stretching-like vibrations of the Mn(Fe)O$_6$octahedra, respectively. The peak that corresponds to the B$_{2g}(1)$ mode is correlated with the JT distortion in the compounds with large ionic radii [33]. The distortion of Eu$_{0.65}$Sr$_{0.35}$Fe$_{0.3}$Mn$_{1+x}$O$_3$ increases as the concentration of iron increases and may lead to an increase in the frequency; this phenomenon is the same as that reported in [26].

The electrical properties of any material are an important factor that reveal important and reliable information about the transport phenomenon and other physical properties of the material. To determine the general behavior of the electrical resistivity and to gather information about the current transport mechanisms, the resistivity data were analyzed to distinguish between the possible mechanisms in the tested samples, namely, band transfer, thermionic emission, thermally assisted tunneling and variable range hopping [34]. The variation in the DC electrical resistivity of
Eu$_{0.65}$Sr$_{0.35}$Mn$_{0.7}$Fe$_{0.3}$O$_3$ as a function of temperature is shown in Figure 5. It is clear that the temperature dependence of the resistivity curve shows that the semiconductor behavior of the resistivity of Eu$_{0.65}$Sr$_{0.35}$Fe$_x$Mn$_{1-x}$O$_3$ decreases with increasing temperature. Attempts were made to fit the semiconducting behaviors to better understand the conduction of the electrons between localized states. The fit of the resistivity curves could clarify the type of conduction, discriminating between pure thermally activated conductivity and variable range hopping (VRH) between localized electronic states.

![Figure 5. DC resistivity – temperature dependence of Eu$_{0.65}$Sr$_{0.35}$Mn$_{0.7}$Fe$_{0.3}$O$_3$](image)

**Figure 5.** DC resistivity – temperature dependence of Eu$_{0.65}$Sr$_{0.35}$Mn$_{0.7}$Fe$_{0.3}$O$_3$

![Figure 6. Dielectric constant of Eu$_{0.65}$Sr$_{0.35}$Mn$_{0.7}$Fe$_{0.3}$O$_3$](image)

**Figure 6.** Dielectric constant of Eu$_{0.65}$Sr$_{0.35}$Mn$_{0.7}$Fe$_{0.3}$O$_3$
For thermally activated conductivity, the electrical resistivity can be written as a function of temperature, T, as follows: 
\[ \rho = \rho_0 \exp\left(-\frac{E_A}{k_B T}\right), \]
where \( \rho_0 \) is a pre-exponential coefficient, \( E_A \) is the activation energy, \( k \) is the Boltzmann constant and \( T \) is the absolute temperature [34]. According to this formula, one can calculate the activation energy, which has a value of 0.498 eV.

From the SEM, XRD and Raman data, one can correlate the increase in the bond length and the activation energy of \( \text{Eu}_{0.65}\text{Sr}_{0.35}\text{Fe}_{x}\text{Mn}_{1-x}\text{O}_3 \) with the increasing iron content, which is similar to Fe substitution at the Mn site in \( \text{Nd}_{0.65}\text{Sr}_{0.35}\text{Fe}_{x}\text{Mn}_{1-x}\text{O}_3 \) [36] and \( \text{SmFexMn}_{1-x}\text{O}_3 \) [37]. Because Fe doping is the direct replacement of Mn\(^{3+}\) by Fe\(^{3+}\), the sites that are now occupied by Fe\(^{3+}\) can no longer effectively participate in the DE process because only the Mn\(^{e_g}\) band is electronically active, within which electron hopping can occur between Mn\(^{3+}\) and Mn\(^{4+}\). Thus, DE is suppressed, resulting in an increase in the resistivity [38].

**Figure 7.** Resistivity - Frequency dependence plots of \( \text{Eu}_{0.65}\text{Sr}_{0.35}\text{Fe}_{0.3}\text{Mn}_{0.7}\text{O}_3 \)
Using the measured capacitance values and the dimensions of the pellet (real part) of the materials, one can calculate
\[ \delta \varepsilon' = \frac{Cd}{\varepsilon_0 A} \]
where \( C \) is the capacitance of the pellet in farad, \( d \) is the thickness of the pellet in meters, \( \delta \varepsilon' = 8.85 \times 10^{-12} \text{ } \)is the permittivity of free space and \( A \) is the cross-sectional area of the cylindrical pellet in \( \text{m}^2 \). The dielectric constant (real part) in the investigated system is contributed by several structural and microstructural factors. The imaginary part of the dielectric constant \( \varepsilon'' \) was calculated using the relation \( \varepsilon'' = \varepsilon \tan \delta \), where \( \tan \delta = \tan (90 - \phi) \) is the dispersion of the dielectric loss tangent. Structural and various electrical properties of polycrystalline \( \text{Ca}_{0.5+\delta} \text{Sr}_{0.5-x} \text{Nd}_{0.5-\delta} \text{Fe}_{0.5} \text{O}_3 \) is studied in ref [39] and it is found that that the composition dependence of lattice parameters, density and microstructural vary significantly with Ca content. The dielectric frequency dependent measurements in [40] showed that the dielectric constant \( \varepsilon' \) increases with increasing Ca content and similarly the dielectric loss \( \tan \delta \) and ac conductivity \( (\sigma_{ac}) \). The high \( \varepsilon' \) observed in [41] samples are similar to our case and these results are suitable for fabrication of devices. The plots of the dielectric constant \( \rho \) with frequency at room temperature for the system \( \text{Eu}_{0.65} \text{Sr}_{0.35} \text{Mn}_{0.7} \text{Fe}_{0.3} \text{O}_3 \) are shown in Figure 7. At lower frequencies, the compound shows different types of polarization (i.e., interfacial, dipolar, atomic, ionic and electronic). A decrease in \( \varepsilon \) was observed with an increase in frequency; this variation can be explained on the basis of space charge polarization. At higher iron concentrations, e.g., \( \text{Eu}_{0.65} \text{Sr}_{0.35} \text{Mn}_{0.7} \text{Fe}_{0.3} \text{O}_3 \), the dielectric constant of the sample depends strongly on frequency, as explained in ref. [20]. The high value of \( \varepsilon \) observed in the \( \text{Eu}_{0.65} \text{Sr}_{0.35} \text{Fe}_{0.5} \text{Mn}_{0.5} \text{O}_3 \) system shows the ferroelectric nature of this system. Voids, dislocations and other defects appear at low frequencies [40-41]. The decrease in the penetration depth of the electromagnetic waves at a high dielectric constant is due to the increase in the skin effect. Figure 7 depicts the frequency variation of loss tangent \( (\tan \delta) \) of \( \text{Eu}_{0.65} \text{Sr}_{0.35} \text{Mn}_{0.7} \text{Fe}_{0.3} \text{O}_3 \) at room temperature. Note that at relatively lower frequencies, the values of \( \tan \delta \) are high and decrease rapidly with increasing frequency. The decrease in \( \tan \delta \) with increasing frequency is attributed to the fact that the hopping frequency of the charge carrier cannot follow the changes of polarity of the external field beyond a certain frequency [41]. Both \( \varepsilon \) and saturated polarizations depend on the grain size of the materials. However, the SEM micrograph shows a granular structure with a dense morphology and little porosity, which offers an abundance of insulating grain boundaries, leading to an increase in the dielectric constant with decreasing grain size. The valance of manganese in \( \text{Eu}_{0.65} \text{Sr}_{0.35} \text{Mn}_{0.7} \text{Fe}_{0.3} \text{O}_3 \) is \( (0.55 \text{Mn}^{2+} + 0.35 \text{Mn}^{4+}) \) and the valance of manganese in \( \text{Eu}_{0.65} \text{Sr}_{0.35} \text{Mn}_{0.5} \text{Fe}_{0.5} \text{O}_3 \) is \( (0.35 \text{Mn}^{2+} + 0.35 \text{Mn}^{4+}) \), where the double exchange phenomenon is complete, whereas in \( \text{Eu}_{0.65} \text{Sr}_{0.35} \text{Mn}_{0.3} \text{Fe}_{0.7} \text{O}_3 \), double exchange is not complete, as indicated by \( (0.35 \text{Mn}^{2+} + 0.15 \text{Mn}^{4+}) \); thus, we found that the resistivity is much higher for concentrations of iron greater than 0.3; see Figure 7.

4. Conclusions
The conduction mechanism in \( \text{Eu}_{0.65} \text{Sr}_{0.35} \text{Mn}_{0.7} \text{Fe}_{0.3} \text{O}_3 \) is thermally activated, where the valance of manganese is considered as half trivalent and tetravalent; \( (0.35 \text{Mn}^{2+} - 0.35 \text{Mn}^{4+}) \). This makes the double exchange phenomenon is complete, whereas in \( \text{Eu}_{0.65} \text{Sr}_{0.35} \text{Mn}_{0.5} \text{Fe}_{0.5} \text{O}_3 \) [33], double exchange is not complete, as indicated by \( (0.35 \text{Mn}^{2+} - 0.15 \text{Mn}^{4+}) \); thus, we found that the resistivity is much higher for concentrations of iron greater than 0.3. The frequency dependence of the dielectric constant of \( \text{Eu}_{0.65} \text{Sr}_{0.35} \text{Mn}_{0.3} \text{Fe}_{0.7} \text{O}_3 \) indicates that space charge polarization contributes significantly to their observed dielectric parameters.

The first-order approximation of the [b] and [c] tilt are calculated to be \( [b]\text{tilt} \sim 5.8^\circ \) and \( [c]\text{tilt} \sim 13.1^\circ \) that is mean that we have more distorted structure than other compounds.
5. Acknowledgement
The author is thankful to the Deanship of Scientific Research for Grant Research code NU/ESCI/14/019 to Dr. I. A. Abdel-Latif, Najran University, Najran, Saudi Arabia. Advanced Materials and Nano Research Center in Najran University is gratefully acknowledged for providing access to the instruments at their facility.

6. References
[1] Coey JMD, Viret M, von Molnar S 1999 Adv. Phys. 48 167
[2] Von Helmolt R, Wecker J, Holzapfel B, Schultz L, Samwer K 1993 Phys. Rev. Lett. 71 2331
[3] Mandal K D and Behera L 2008 J. Alloys & Comp. 448 313
[4] Ahmed AM, Saleh S A, Ibrahim EMM, Mohamed H F 2006 Journal of Magnetism and Magnetic Materials 301 452
[5] Jin S, Tiefel T H, Cormack M Mc, Fastnacht P A, Ramesh R, and Chen L H 1994 Science 264 413
[6] Zemni S, DhahriJa, Cherif K, Dahari J, Oumezzine M, Ghedira Mand Vincent H 2005 J. Alloys & Compd. 392 55
[7] Hwang H Y, Cheong S W and Ballogg B 1996 Appl. Phys. Lett. 68 3494
[8] Shankar K S, Kar S, Raychaudhuri K and Subbanna G N 2004 Appl. Phys. Lett. 84 (6), 993
[9] Wang L M, et al., 2007 J. Appl. Phys. 102 023915
[10] Millis A J, Nature 1998 392 147.
[11] Urushibara A, Moritomo Y, Arima T, Kito G, and Tokura Y 1995 Phys. Rev. B51 14103
[12] Bashkirov Sh Sh, Parfenov V V, Valiullin A A, Khramov A S, Trounov V A, Smirnov A P, Abdel-Latif I A 2003 Izv. RAS, Physical Series 67 No 7, p 1072, (in Russian)
[13] Aguadero A, Perez-Coll D, de la Calle C, Alonso J A, Escudero M J, Daza L 2009 J. Power Sources 192 132
[14] Abdel-Latif I A, HassenA,Zybill C, Abdel-Hafiez M , Allam S, El-SherbiniTh 2008 J. Alloys & Compd 452 245
[15] Bhide VG, Rajoria DS, Rama Rao G, Rao CN 1972 Phys. Rev. B6 1021
[16] Raccah P, Goodenough J B 1967 Phys. Rev. 155 932
[17] Ganguli P, Rao C N R 1973 Mate. Res. Bull. 8 405
[18] Zheng G H, Sun Y P, Zhu X B, Song W H 2006 Solid Commun. 137 326
[19] Ahmed M A, ImamN G, AbdelmaksoudM K, SaeidYA 2015 Journal of Rare Earths, 33 965–971
[20] Abdel-Latif I A, Ismail A A, Bouzid H, Al-Hajry A 2015 Journal of Magnetism and Magnetic Materials 393 233
[21] Abdel-Latif I A, Saleh SA 2012 Journal of Alloys and Compounds 530 116
[22] Martinez B, Balcells L, Fontcuberta J, CohencaC H and Jardim R F 1998 J. Appl. Phys, 83 7058
[23] Uusi-Esko K, Malm J, Imamura N, Yamauchi H, Karpipinen M 2008 Mater. Chem. and Phys. 112 1029
[24] Shannon R D and Prewitt C T 1969 Acta Crystallogr. B25 925
[25] Channu VSR, Holze R, Wicker Sr S A, Walker Jr E H, Williams QL, Kalluru R R 2011 Mater. Sci. Appl. 2 1175
[26] Rodriguez-Carvajal J, 1993 Physica B192 55
[27] Ahmed Farag I S, Mostafa A M and Abdel-Latif I A 2007 Egypt. J. Solids, 30 149
[28] Iliev M N, et al., (1998) Phys. Rev. B57 2872
[29] Yoon S, Liu H L, Schollerer G, Cooper S L, Han P D, Payne D A, Cheong S-W, and Fisk Z1998 Phys. Rev. B58 2795
[30] Liarokapis E, Leventouri Th, Lampakis D, Palles D, Neumeier J J, and Goodwin D H1999 Phys. Rev. B 60 12758
[31] Granado E Sanjurjo J A, Rettori C, Neumeier J J,Oseroff S B2000 Phys. Rev. B 62 11304
[32] Choi K-Y et al.,2003 J. Phys. : Condens. Matter15 3333
[33] Martin-Carron L de Andrés A 2001 J. Alloys & Comp.323-324 417
[34] Abdel-Latif I A2011 AIP Conf. Proc.1370 108
[35] Abdel-Latif I A et al 2006 Egypt. J. Solids, 29 341
[36] Bashkirov Sh Sh Parfenov VV Abdel-Latif IAZaripova LD 2005 J. Alloy. & Compd.,387 70–73
[37] Li Y., et al, 2007 J. Alloys & Comp. 441 1
[38] Hussain S., et al, 2006 J. Crys. Grow.297 403
[39] Nikola I. Ilić, Adis S. Džunuzović, Jelena D. Bobić, Bojan S. Stojadinović, Peter Hammer, Mirjana M. VjatovićPetrović, Zorana D. Dohčević-Mitrović, Biljana D. Stojanović, 2015 Ceramics International41 69
[40] Shah M R, Akther Hossain A KM 2013 Journal of Materials Science &Technolog. 323–329