Preparation and Structural Characterization of $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$

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The present work deals with the structure study of $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$ (x= 0.1, 0.5, and 0.7) by X-ray diffraction. These compounds were prepared from pure 99.9% oxides using standard solid state reaction. The final sintering temperature was 1350°C for 72 h. The X-ray analysis showed that all samples have a single perovskite structure phase, which crystallizes in orthorhombic system with space group Pbnm. An increase in the lattice volume was found upon increasing the iron concentration. The mean bond length (Mn/Fe – O) increases linearly with increasing the iron content. Less distortion in MO_6 octahedron is obtained for low iron content (x=0.1).

1. Introduction:

In the recent years, there has been a lot of interest in rare earth manganese perovskites due to their potential and technological applications and the fascinating physical phenomina they exhibit, such as clossal magnetoristance (CMR), metal-insulator (MI) and charge ordering (CO) [1-3]. Since 1950, the unusual electrical and magnetic properties for such compounds are very interesting subject because the striking correlation between them [4, 5]. The interplay between magnetic, transport and structural properties gives rise to the above-mentioned complex phenomena. One of the most extensively studied system is $R_yA_{1-y}MnO_3$, where R is a rare earth element, A is a divalent element like Ca, Sr, Ba, …. They crystallize with an orthorhombic distortion perovskite-like structure [6]. The R sites are surrounded by distorted 12 oxygen atoms polyhedra while the oxygen octahedra around the Mn ones are less distorted. When an octahedron is tilted in some particular way, it causes tilting of the neighboring octahedra [7]. This tilt in octahedra is very important in defining the magnetic and electric exchange interaction between transition

metal elements e_g and Oxygen $2p$ orbitals of such compounds. The simple formula of both [b] and [c] tilt were given in ref. [7]; [b] tilt ~ $(180-\alpha)/2$ and [c] tilt ~ $(180 - \beta)/2$, where α and β are the angles: $M – O1 – M$ and $M – O2 – M$, respectively (M is the transition metal cation Fe or Mn). The thermal treatment during preparation of such compounds may lead to the difference in the tilt of MnO_6 octahedra for the same compound. For example, the lattice constants of $Sm_{0.6}Sr_{0.4}MnO_3$ which prepared using solid state reaction in different Laboratories, as reported in ref [8] and ref [9], are the same. The difference was found only in the bond length of Mn – O and the value of magnetoresistance MR. The less distortion in the MO_6 octahedra may lead to the increase in the magnetoresistance value. The importance of determining the tilt angles is quite clear in describing some physical properties like the magnetoresistance.

The unusual electrical and magnetic properties of such compounds are strongly correlated with their structure. Therefore**,** the **s**tudy of crystal structure characterization and its relation with the substitution of manganese by iron is represented in the present paper.

2. Experimental Details:

A series of $Eu_{0.65} Sr_{0.35} Mn_{1-x}Fe_xO_3$, x = 0.1, 0.5 and 0.7 were prepared using the solid state reaction method from the initial pure 99.9% oxides (Eu_2O_3, Fe_2O_3, Mn_2O_3 and SrO). These compounds were well mixed with appropriate ratios using agate mortar and pressed in disk form under a pressure = 15 ton/cm^2. The obtained disks were fired at 1200°C for 12 h in air. The presintered samples were ground again and pressed under the same pressure in the form of disk with 12 mm diameter. The samples were fired again at 1350°C for 72 h with an intermediate grinding to ensure homogenization, these heat treatment was followed by natural furnace cooling.

To ensure the phase formation, the structure of the solid solutions was investigated at room temperature by means of powder X-ray diffraction method using Diano diffractometer with filtered Co-Kα radiation operated at 45 kV and 9 mA. The scanning range was $2\theta = 20\text{-}100°$. X-ray diffraction of all samples were performed using step scan mode with step size = 0.02 and step time = 5 min. The crystal structures were refined by the Reitveld method of whole pattern fitting using Fullprof program [10]. The experimental profiles were fitted with modified Thompson Cox Hasting Pseudo Voigt function. Annealed quartz standard sample, delivered from Diano Corporation, has been used to determine the zero shift and the instrumental profile utilizing the same scanning conditions as that performed for the investigated samples.

3. Results and Discussions:

The X-ray diffractograms are shown in Fig. (1). It was found that the $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$ samples with x = 0.1, 0.5 and 0.7 consist of one phase single perovskite of orthorhombic system that matched with the ICDD card No. (82-1474).. The X-ray diffraction patterns of all samples were refined with Rietveld method to calculate the accurate unit cell dimensions, using the space group P_{bnm}, Z = 4 with A site cations (Sr/Eu) situated at Wyckoff position 4c (x, y, 1/4), B-site cations (M = transition metal cations Mn and/or Fe) situated at Wyckoff position 4b (0.5, 0, 0) and two oxygen atoms O1 and O2 situated at 4c and 4d Wyckoff positions, respectively. A full profile analysis included a refinement of background, scaling factor, lattice parameters, Brag peak profile, positional and thermal parameters were done. The overall good agreement between the calculated and observed patterns for $Eu_{0.65}Sr_{0.35}Mn_{1-x}Fe_xO_3$, x = 0.1, 0.5 and 0.7 is illustrated in Fig. (2). The agreement factors show that the refinement procedures are acceptable for all samples. All the crystallographic data obtained after the refinement of the structure of the investigated samples are summarized in Table (1). It is obviously that the volume of unit cell is increased with increasing the iron contents. This small increase seems to be due to the difference between the ionic radii of iron ($Fe^{+3} = 0.55$Å) and manganese ($Mn^{+4} = 0.53$ Å).

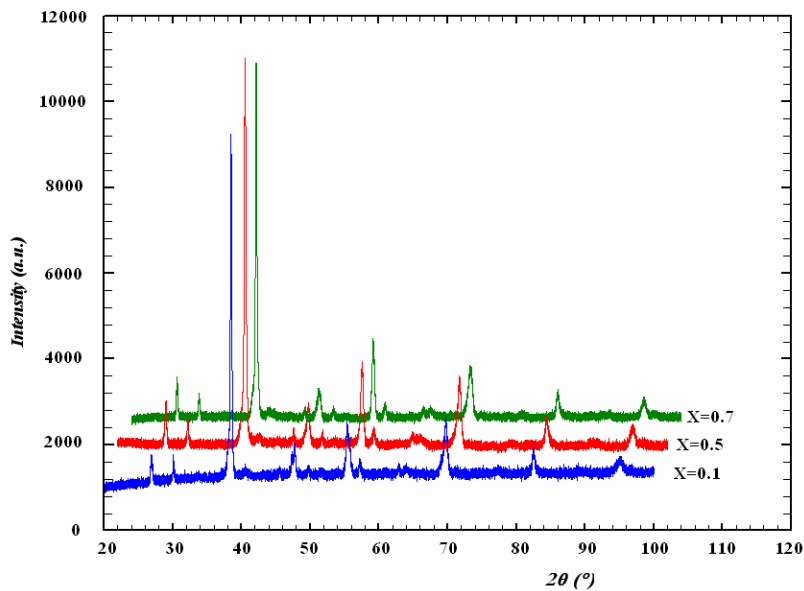**Fig. (1):** X-ray diffraction patterns of $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$.

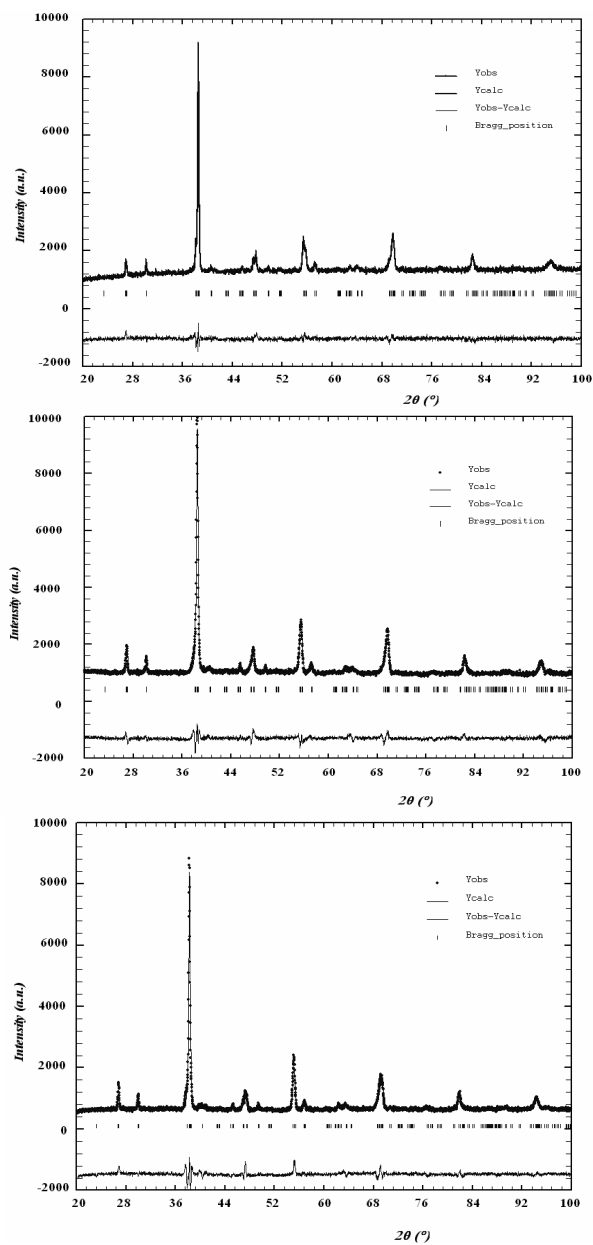**Fig. (2)**: X-ray diffraction data and calculated pattern for $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$. The experimental data are shown as filled circle, the calculated fits and difference curves as solid lines. Tick marks indicate the calculated positions of peaks.

Table (1): The Lattice parameters, the volume of unit cell and the coordinates of $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$.

| x	a (Å)	b (Å)	c (Å)	V (Å^3)	Atom	x	y	z
0.1	5.4134	5.4768	7.6513	226.847	Eu/Sr	-0.0012	0.0379	0.25
					Mn/Fe	0.5	0.0	0.0
					O1	0.0530	0.4754	0.25
					O2	-0.2585	0.2648	0.0492
0.5	5.4157	5.4806	7.6714	227.698	Eu/Sr	-0.0006	0.0385	0.25
					Mn/Fe	0.5	0.0	0.0
					O1	0.0708	0.4616	0.25
					O2	-0.2842	0.2759	0.0542
0.7	5.4395	5.5143	7.7164	231.467	Eu/Sr	-0.0025	0.0394	0.25
					Mn/Fe	0.5	0.0	0.0
					O1	0.0940	0.4560	0.25
					O2	-0.2690	0.2650	0.0395

Using the refined coordinates of each ion, the bond lengths of cations M (Fe/Mn) – anions (Oxygen O1 and O2) and the M – O1 – M and M – O2 – M angles were calculated and listed in Table (2). The mean bond length of M – O increases linearly with increasing the iron content x in the $Eu_{0.65}Sr_{0.35}Fe_x Mn_{1-x}O_3$ samples as shown in Fig. (3). This increase in bond length may explain the increase in the resistivity of the $Nd_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ with the increase in the iron content as reported by Abdel-Latif *et al.* [5].

The octahedral tilt of the perovskite structure has a significant meaning, which describes the charge and magnetic transfer. The α, β and the octahedral tilt angles ([b] and [c] tilt angles) are given in Table (2). From the values the octahedral tilt angles, it is noticed that the less distortion in MO_6 octahedron is observed for the less content of iron (x = 0.1).

Table (2): The M – O bond length and M – O1 – M and M – O2 – M, [b] tilt and [c] tilt angles in $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$.

x	0.1	0.5	0.7
M-O1 (Å)	1.939(1)	1.967(3)	2.010(4)
M-O2 (Å)	1.931(7)	1.957(11)	1.951(16)
M-O2 (Å)	1.996(7)	2.011(11)	1.978(16)
∠M-O1-M (°)	161.18(6)	154.25(14)	147.38(18)
∠M-O2-M (°)	157.4(3)	152.3(4)	160.5(7)
[b] tilt (°)	9.41	12.88	16.31
[c] tilt (°)	11.3	13.85	9.75
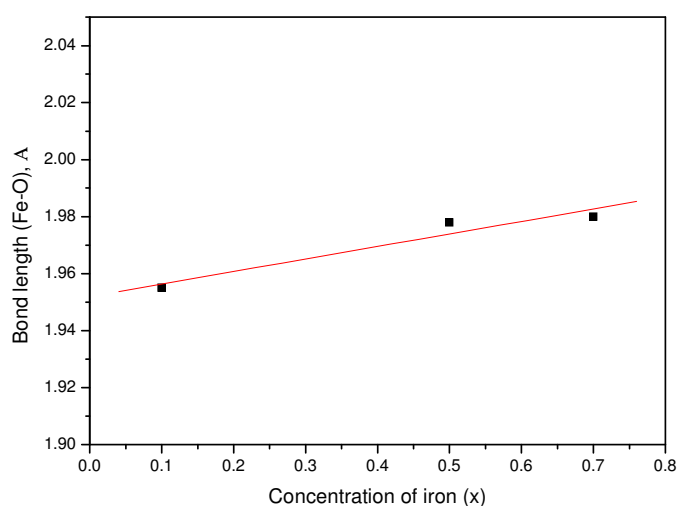
Fig. (3): M – O bond length dependent on the iron concentration x for $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$.

Conclusions

A single perovskite phase of orthorhombic system was achieved for $Eu_{0.65}Sr_{0.35}Fe_xMn_{1-x}O_3$ compounds. The volume of unit cell and the M – O bond length increase linearly with iron concentration x. The less distortion in MO_6 octahedron is obtained for low iron content of x =0.1.

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