INVESTIGATION ON STRUCTURE AND POSSIBLE MAGNETIC PHASE IN SN-DOPED $LA_{2/3}CA_{1/3}MNO_3$

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ABSTRACT

The substitution of high Tin (Sn) doping concentration by 10%, 20% 30 % and 40% have been made primarily by Solid state reaction (SSR) methods to study structure and magnetic phase properties of $(La_{1-x}Sn_x)_{1/3}Ca_{2/3}MnO_3$. The XRD, shows all samples in single phase with orthorhombic structure ,the microstructures were studied via scanning electron microscope (SEM), which indicated that grain size increasing as increasing of Sn doping. Magneto-resistivity dependence to the temperature (MR_T).) was measured by standard four-probe system A decrease in temperature was seen at the phase transition temperature (TP). and the resistivity decreased sharply among substitution $Sn2^+$ for La^{2+} ions increases from 10 % to 40 %. The temperature- dependence magneto resistance (M–T) shown the high MR% of the samples were around the TC temperature, which can be explained by enhancement of DE interaction between Mn^{+3} - Mn^{+4} ionic.

Keywords: XRD, CMR, Manganites, Susceptibility, magnetic Properties Curie temperature

1. INTRODUCTION

Recently, the perovskite manganite La1-xAxMnO3 where (A = Ca, Sr, Ba) have been studied extensively. The researches interest in these materials is related to their magnetic, electrical properties and effect of colossal magneto resistance (CMR) [1-3] dubel exchange interaction[4]. The most interesting CMR Materials Numerous technical applications, including magnetic data storage, read-write heads, magnetic-bolometric sensors, magnetic tunnel junctions, and magneto resistive random access memory (MRAM), depend on magneto-resistance (MR). [1, 5]. In these materials the electron coupling and double exchange interaction (DE) are play the main

role in occurrence interesting phenomena such as insulator-metal transition, ferromagnetism (FM) and colossal magneo resistance (CMR)[6, 7]. The average size of La^{+3}inos has been substituted by small percentage of smaller ionic size of Sn^{+2}.

The previous studies have showed that the structural, magnetic and electrical transport properties of manganites are closely related with preparation method and conditions. There are some methods to synthesize the perovskite manganite $La_{1-x}A_xMnO_3$., but the most suitable method is (SSR) solid-state reaction of the components [1, 6, 8]. Controlling the temperature during the solid state reaction is one of the major problems. In addition, the solid state reaction method requires high annealing temperature (from 1200 C^0 to 1400 C^0) and long sintering time (> 10 h) to achieve high homogeneity and purity.

This article examined (Sn) to substitute in (La). On one hand, Sn has effective magnetic moment (μeff = 1.5 μB) , where μ B is Bohr magneton, which will cause (Tc) and magnetization to strengthen. On the other hand, the ion radius of Sn(1.13 Å) <sn> is smaller than that of La(1.16 Å)[8]. The structure were investigated by Rietveld refinements of powder X-ray .An investigation on the influence of La+3 substitution by Sn+2 on the structure .The PCR studied with applied Rietveld full-profile method by usig the FULLPROF software package[7]. Using a JEOL 6400 scanning electron microscope (SEM), the size and arrangement of the grains were studied. The magneto-resistance measurements were performed using magnetometer system in a temperature range from 150 to 300 K with maximum magnetic field about one T was applied.

2.EXPERIMENTAL

Bulk polycrystalline$(La_{1-x}Snx)_{2/3}Ca_{1/3}MnO_3$ with x=0.0, 0.1, 0.2, 0.3 and 0.4 compound was created via standard solid state reaction (SSR) employing stoichiometric amounts of precursors, La_2O_3, $CaCo_3$, SnO_2, and MnO_3, all of which had purity levels about 99.99%. Before weighting, La_2O_3 was carefully dried by per-heating at 700 0C for 12 hours. High purity acetone was utilized to facilitate the precursor mixing procedure. After being dried and homogenized, the powder was crushed, compressed, and calcined for 24 hours at 900 0C .The resulting mixtures were pressed into pellets and sintered at 1300oC for 24 hours in air. The sintering result pellets were reground into very fine powder and used in this study.

The XRD pattern were collected at room temperature using diffractometer (using Phillips PW1830) with CuKαradition (λ=1.5418 Å) at 40 KV, 30 mA was used to examine the structure of the sintered powder samples. Powdered samples were scanned in the rang 2θ of 100 to 800. Scanning electron microscopy (SEM) was used to examine the surface morphology of the samples. The fractured surface of the sample was coated with evaporated gold prior to insertion into the microscope. JEOL 6400 scanning electron microscopy was used. The main purpose of this analysis is to study the correlation between microstructure features such as porosity, necking, agglomerate, homogeneity and grain size related to the electrical and magnetic properties of the samples.

A Four Prop Point System was utilized to measure the temperature dependences of magnetization and magneto-transport characteristics, with a maximum applied field strength of 1.05 Tesla

3. RESULTS AND DISCUSSIONS

The XRD analysis display I table (1 and 2) .Figure1 Shows the X-ray diffraction pattern of powder samples $(La_{1-x}Sn_x)_{2/3}Ca_{1/3}MnO_3$ with x=0.0, 0.1, 0.2, 0.3 and 0.4. XRD patterns analysis show that, all the samples keep in very good single phase, the crystal structure orthorhombic symmetry. As the Tin concentration increase as the cell unit volume decrease, because the ion radius of Sn (0.113 nm) is smaller than that of La (0.116 nm). Examined Fitting h k l reflection and the extinction rule for the given space group (62 P n m a) were used to identify the peaks. All of the samples under the (O_2) flow are found to be single-phase materials. Also, for the sample with a high Sn+2 content, some peaks' intensities increase and their widths (HWFM) decrease. This implies that following high-temperature sintering, a greater. This clearly suggests that during the high temperature sintering process, the material as a whole developed a more crystalline structure.

TABLE I: SHOWS THE UNIT CELL VOLUME AND THE LATTICE PARAMETERS A, B, AND $(La_{1-X}Sn_X)_{2/3}Ca_{1/3}MnO_3$ SAMPLES WITH X=0.0,0.1, 0.2, 0.3 AND 0.4

Sn Concentration	lattice parameters				Volume density (gm/cm3(
	a (Å)	b (Å)	C (Å)	Volume $(Å)^3$	
0.0	5.382	7.377	5.825	231.27006	6.39
0.1	5.425	7.698	5.489	229.2297	6.38
0.2	5.385	7.657	5.523	227.72956	6.75
0.3	5.391	7.661	5.485	226.53297	6.84
0.4	5.381	7.656	5.481	225.8004	6.84
System	Orthorhombic				
space group	62 P n m a				

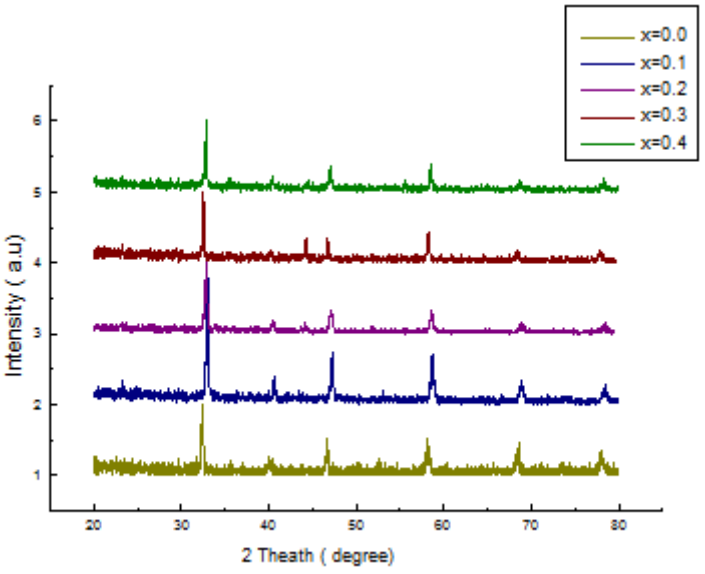

Fig. 1. XRD patterns (La1-x Snx)0.67Ca0.33 MnO3 for all samples

TABLE 2: DISPLAY ASYMMETRIC UNIT: 5 ATOMS $La_{2/3}Ca_{1/3}MnO_3$

Label	**Type**	**X**	**Y**	**Z**
Mn1	Mn	0.000	0.000	0.000
La1	La+2	0.0187	0.25	0.9932
Ca1	Ca+2	0.0187	0.25	0.9932
O1	O2-	0.491	0.25	0.061
O2	O2-	0.2757	0.0339	0.724
Bond distance (Å)				
MnMn	3.84108	3.8457	3.8527	3.86020
MnO1	1.96023	1.96095	1.95519	1.96394
MnO2	1.83261	2.01147	2.13992	1.96424
Bond angles (°)				
MnO1Mn	155.780	156.365	161.368	157.546
MnO2Mn	165.0235	163.2664	161.4558	160.9988

In order to obtain further information about grain morphology, of $(La_{1-x}Sn_x)_{2/3}Ca_{1/3}MnO_3$ with x=0.0, 0.1, 0.2, 0.3 and 0.4 were examined by SEM. The microstructure of polycrystalline samples of (La1-x Snx) 0.67Ca0.33 MnO3 with x= 0.0, 0.1, 0.2, 0.3 and 0.4 are display in Figure 2 (A), (B), (C) and (D) respectively. The electron micrograph was obtained on fracture

surface samples with magnification bout 2000X. Although, the particle size generally varies in a broad range from nm scale to a few μm, the samples that have been subjected to study consist mainly of small particle of nanometers order and the most of these small grains have nearly spherical shape. The SEM images showed that the grain size of all samples is enhanced as Tin concentration is increasing. Moreover, there is an sudden change in the grain size and grain boundaries for sample with 40 % it has very small melted where no clear boundary observed.

The substituted of Sn in $La._{2/3}Ca_{1/3}MnO3$ with x=0.0, 0.1, 0.2, 0.3 and 0.4 rare-earth manganite's, Exhibit very interesting magnetic properties [1]. Maximum ferromagnetic Curie temperature is observed when x=0.0 in $La_{2/3}Ca_{1/3}$ MnO_3 [1, 4] and anti-ferromagnetic when x=0.1 is about (86 K) [5]. At a doping level of x=0.2, Tc is around 78 K above Tc the material is insulator, and the transition at Tc is metal to ferromagnetic to paramagnetic [5, 6, 9].

The magnetic characteristics of these manganite's have been explained through the Mn^{+3}-O-Mn^{+4} exchange mechanism, which is influenced by the distortion of perovskite structures due to varying ion sizes and the electron-phonon coupling caused by the Jahn Teller effect of Mn 3 ions. This has been documented in previous studies [3, 10-12]. Zener has described the Mn^{+3} and Mn^{+4} ions as having itinerant and localized electrons in orbital configurations of t_{2g} e_{1g} and t_{2g} e_{0g}, respectively [5, 6].

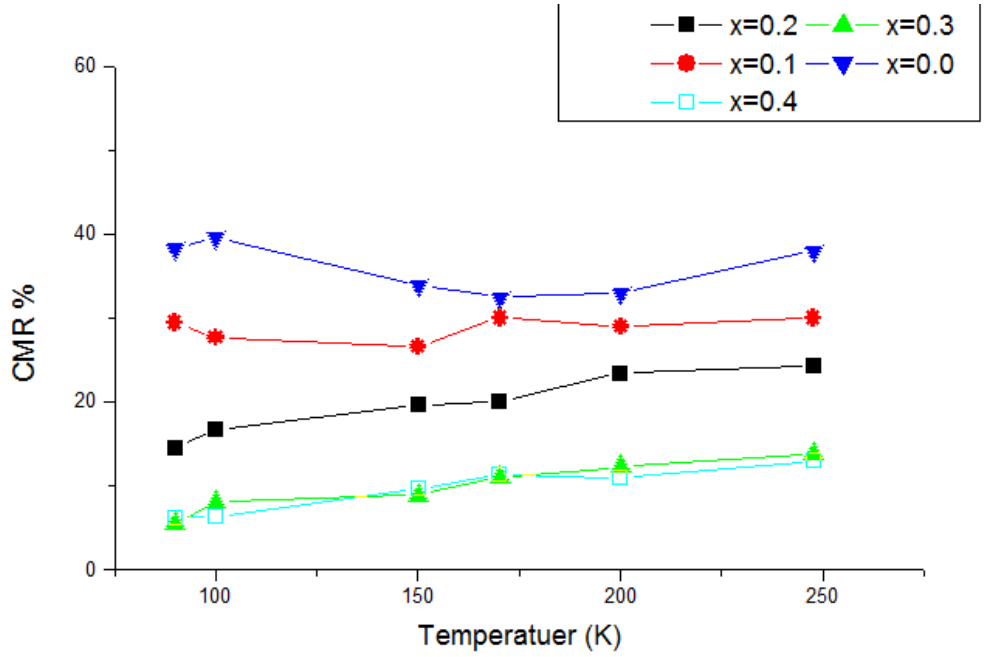

Fig 3: CMR at different temperature for $(La_{1-x}Sn_x)_{2/3}Ca_{1/3}MnO_3$with x=0.0, 0.1, 0.2, 0.3 and 0.4

Colossal magnetoresistance(CMR) an unusually large change of resistivity observed in certain materials $(La_{1-x}Sn_x)_{2/3}Ca_{1/3}MnO_3$with x=0.0, 0.1, 0.2, 0.3 and 0.4 with an applied of magnetic field about 1.06 T.

The CMR ratio is defined as

$$MR\% = \frac{R(H) - R(0)}{R(0)} \times 100$$

Where RH is the resistance in the present of magnetic field and R0 is the zero field resistance.

In $La_{2/3}Ca_{1/3}MnO_3$perovskite,T_C sensitively changed with Sn concentration increases this can be accomplished by doping the perovskite structure with trivalent rare-earth ions of various ionic sizes[1, 5, 9, 13]. Local structural characteristics like the Mn–O bond distance and Mn–O–Mn bond angle are altered by the Sn substitution in La, and these changes have an immediate

impact on the situation where electrons hop between Mn ions, or the electronic band this can be accomplished by doping the perovskite structure with trivalent rare-earth ions of various ionic sizes [1, 5, 9, 13]. Local structural characteristics like the Mn–O bond distance and Mn–O–Mn bond angle are altered by the Sn substitution in La, and these changes have an immediate impact on the situation where electrons hop between Mn ions, or the electronic bandwidth. We find that the CMR effect in low T_C can be explained by hopping electron through Mn^{+3}-O-Mn^{+4} on the neighboring ferromagnetic domains' relative spin orientation, which is controllable by applying magnetic fields [5].

4. CONCLUSION

This work investigates the effect of replacing La+3 with Sn+2 on the ferromagnetic phase transition in $La_{2/3}Ca_{1/3}MnO_3$. By using measurements of magnetism and X-ray diffraction techniques. Series of pure orthorhombic $(La_{1-x}Sn_x)_{2/3}Ca_{1/3}MnO_3$samples with x= 0.0, 0.1, 0.2, and 0.3 were prepared via solid-state reaction. As Tin (Sn) concentration increases the unit cell volume decrease all samples exhibit decrease of antiferromagnetic ordering temperature with increasing (Sn) content. According to magnetic measurements, the Curie temperature drops as the concentration of Sn rises

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