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Synthesis and Characterization of $La_{1-X}Bi_XCa_{1-Y}Sr_YMnO_3$ CMR Manganites

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Abstract: Manganese perovskites have been the subject of renewed interest because of the discovery of colossal magnetoresistance (CMR). For $La_{1-x}Ca_xMnO_3$ (LCMO) a rich phase diagram has been revealed as a function of temperature and doping content (x), which is due to the intricate interplay between charge, spin, orbital and lattice degrees of freedom. Of the several combinations explored until recently, LCMO has attracted wide attention due to its significant colossal magneto resistance effect, intermediate bandwidth, and exhibition of stable orthorhombic phase for all values of x. In the present investigation, $La_{1-x}Bi_xCa_{1-y}Sr_yMnO_3$ (LBCSMO) samples are synthesized by low temperature nitrate route method. The composition and structural properties are studied at various concentrations by X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). The structural analysis shows that the LBCSMO is crystallized in an orthorhombic perovskite structure belonging to Pnma space group. The crystal size of the sample is calculated using Scherrer formula and the unit cell volume is observed to be increase with increasing Bi concentration. The morphology of the samples is studied and the corresponding grains are observed to be spherical in shape. The compositional studies show that the atomic percentages of elements are nearly stoichiometric.
Keywords: manganites; metal - insulator transition; magneto-resistance.

Introduction and Experimental

The manganites of type $R_{1-x}A_xMnO_3$ (where R is a rare earth metal: La, Pr, Nd, Dy and A is an alkaline earth: Sr, Ca, Ba, Pd) have attracted much attention because of intermediate e_g electron bandwidth, exhibition of stable orthorhombic phase, charge ordering (Mn^{3+}/Mn^{4+}), etc.[1]. Generally CMR has been found to occur at temperatures very close to Curie temperature (T_C) in $R_{1-x}A_xMnO_3$ manganites, where there is a transition from insulator paramagnetic (PM) to metallic ferromagnetic (FM) phase. At temperatures above T_C, the conducting mechanism in these compounds has been observed to be of semiconducting in nature in contrast to metallic state exhibited at temperatures below T_C. This metallic behavior is favoured by the electron hopping process due to spin alignment of ferromagnetic state. The later behavior is usually explained by the so called double–exchange (DE) mechanism of Zener [2], which involves hopping of e_g electrons between Mn ions when the system is ferromagnetically coupled. Among the variety of manganite perovskites reported in the literature, manganite systems containing trivalent Bi ions particularly show high Curie temperature sand substantial CMR effect. In fact the current aim is to push T_C value well beyond room temperature in order for these compounds to be suitable for practical applications such as magnetic sensors, hard disks, infrared detectors and microwave-based applications [3-4]. In Bi based manganite systems it has been confirmed that Bi^{3+} plays the same role as

the La^{3+} ion in contrast to highly polarizing $6s^2$ lone pair of the Bi^{3+} ions producing different features or behavior in some other compounds [5]. In the present investigation, the effect of Bi^{3+} ion in $La_{1-x}Bi_xCa_{1-y}Sr_y$ MnO_3 (LBCSMO) compounds at various concentrations has been studied. The XRD patterns of all the samples are recorded using a PANalytical X'pert Pro diffractometer. The surface morphology is characterized by Scanning electron microscope (Carl Zeiss EVO50). The compositional analysis is studied using Energy Dispersive Spectroscopy (Oxford instruments Inca Penta FET x3).

Results and Discussion

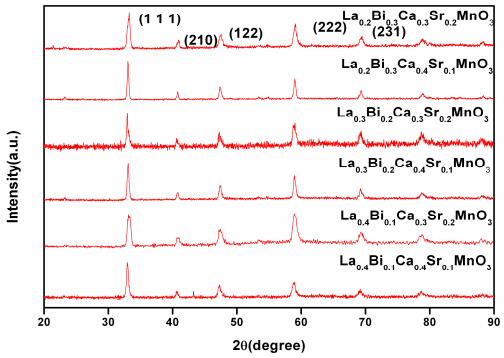

Fig.1. X-ray Diffraction patterns of $La_{1-x}Bi_xCa_{1-y}Sr_yMnO_3$ ($0.1 \le x \le 0.3$, $0.1 \le y \le 0.2$).

Table.1. Variation of lattice parameters with doping concentration.

Lattice parameters	X=0.1,y=0.1	X=0.1,y=0.2	X=0.2,y=0.1	X=0.2,y=0.2	X=0.3,y=0.1	X=0.3,y=0.2
a (Å)	4.761	4.696	4.696	4.7	4.679	4.685
b (Å)	4.385	6.509	6.596	6.593	6.741	6.754
c (Å)	5.063	3.801	3.806	3.834	3.778	3.806
Volume $(Å)^3$	105.7	116.1	117.8	118.8	119.16	120.4

The structural characterization of $La_{1-x}Bi_xCa_{1-y}Sr_yMnO_3$ ($0.1 \le x \le 0.3$, $0.1 \le y \le 0.2$) samples is carried out by X-ray diffraction (XRD) analysis and the corresponding XRD patterns are shown in Fig.1. Analysis of these patterns reveals single phase orthorhombic structure with Pnma space group for all the samples. The highest intensity diffraction peak of samples has been found to occur at about (2θ=) 32.6° for reflections from (111) plane along with other reflections corresponding to planes such as (210), (122), (222), (231). The crystallite size of the synthesized samples is calculated using Debye -Scherrer equation ($L = K\lambda/\beta\cos\theta$). The average crystallite size of all samples is estimated to be around 34 nm. In order to study the variation of lattice parameters of samples with composition parameter (x), the same has been estimated using a standard software package. The XRD patterns of all samples could be indexed to orthorhombic structure. The estimated values of lattice parameters and cell volume are given in Table 1. It is clear from that the estimated values of lattice parameters gradually increase with increasing Bi concentration and correspondingly the unit cell volume of samples increases. Also as expected, the larger size of Bi^{3+} ions has resulted in the increase of unit cell volume and consequently less distorted orthorhombic structures for the samples [6].

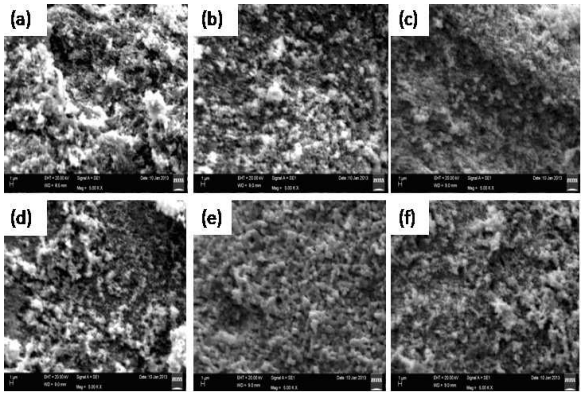

Fig.2. SEM images of $La_{1-x}Bi_xCa_{1-y}Sr_yMnO_3$ ($0.1 \le x \le 0.3$, $0.1 \le y \le 0.2$).

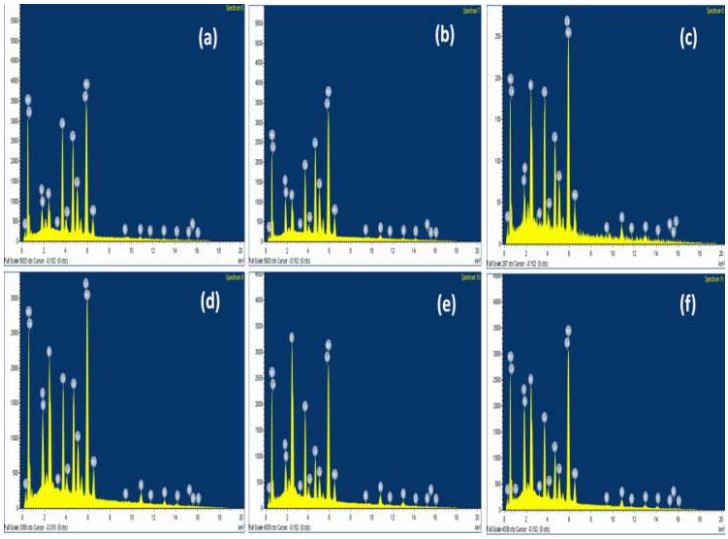

Fig.3. Elemental analysis of $La_{1-x}Bi_xCa_{1-y}Sr_yMnO_3$ $(0.1 \leq x \leq 0.3, 0.1 \leq y \leq 0.2)$.

It is also known that the grain size and morphology plays a critical role in electronic and magneto transport properties in manganite compounds. To elucidate the same, the surface morphology and composition analysis on the other hand are respectively studied using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The study of SEM images reveal that the grain sizes are uniform and nearly spherical in shape as shown in Fig.2. It is to be stressed that crystallite size is smaller than the grain size as grains are composed of several crystallites due to internal stress or defects in the structure. The EDS plots of samples are shown in Fig.3. EDS analysis reveals that the synthesized samples are stoichiometric in composition and no other impurities are present in all compositions.

Conclusions

$La_{1-x}Bi_xCa_{1-y}Sr_yMnO_3$ was synthesized by nitrate route method. The structural characterization reveals that the Bi doped $La_{1-x}Bi_xCa_{1-y}Sr_yMnO_3$ composition has orthorhombic structure with (Pnma) space group. The lattice parameter was observed to be increased with doping concentration. The SEM images show that the particles are nearly spherical shape. The EDS analysis reveals that the synthesized samples are stoichiometric in composition and no other impurities are present in all compositions.

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