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Influence of Grain Size on Structure, Electrical Transport and Magnetoresistive Properties of Nanophasic $\text{La}_{0.8}\text{Na}_{0.2}\text{MnO}_3$ Manganite

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Abstract: A systematic investigation on the $\text{La}_{0.8}\text{Na}_{0.2}\text{MnO}_3$ (LNMO) perovskite had been undertaken, mainly to understand the influence of grain size on the structural, electrical transport and magneto-resistance properties of this material. We have synthesized LNMO samples using modified sol-gel technique at different sintering temperatures (600 & 1000 °C). The structural analysis was performed by using X-ray diffraction (XRD) in terms of lattice parameter variation, unit cell volume and crystallite size (using Scherrer's formula). The analysis of XRD patterns shows that both the samples exhibit rhombohedral crystal system with space group $R\bar{3}c$. AFM was used to obtain actual grain size. AFM results suggest that as the sintering temperature increases, average grain size increases. The electrical resistivity was studied using four-probe method and metal-insulator transition behavior was observed in both the samples. The transition temperature (T_{MI}) is strongly affected by particle size and increases with sintering temperature. The isothermal measurements were carried out between 0 T to 8 T at 5 K and 300 K to understand the magneto-resistance behavior. This novel method also has other potential advantages over other traditional processing techniques such as better homogeneities, lower processing temperature, less sintering time of few minutes and improvement in the material properties.

Keywords : CMR; manganite; sintering temperature; Na doping; XRD.

Introduction and Experimental:

The perovskite manganites with general formula $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$ (where RE = rare earth, A = Ca, Sr, Ba, Pb etc.) have drawn considerable attention, due to their spintronics and sensing applications. The resistance of such materials changes drastically by application of magnetic field. These materials are called colossal magneto-resistance (CMR). CMR properties of such type of perovskite materials can be understood by remarkable phenomenon occurring in these systems such as Jahn-Teller distortion, double exchange mechanism, spin ordering and magnetic ordering [1]. It was found that the substitution of various ions at different sites with various atomic radius and synthesis process can use to influence the structural, electrical and magneto-resistive properties of such manganite systems [2-4]. Moreover, it is suggested that large low-field MR (LFMR) can be obtained when the crystallite size is decreased to nano-scale, which is interesting for fundamental research as well as for potential applications [5]. In the present study, Na^{+1} is selected as monovalent doping at La site in LaMnO_3 compound. In this case, it is possible to obtain an equal amount of hole doping with half the number of the monovalent doping, because the hole density is twice that of divalent ion doping.

Manganite samples of $\text{La}_{0.8}\text{Na}_{0.2}\text{MnO}_3$ were synthesized via the sol-gel method. The required amounts of high purity acetates of La, Na and Mn were dissolved in double distilled water to form an aqueous solution. An equal amount of ethylene glycol was added to this solution with continuous stirring. This solution was heated on a hot plate at a temperature of $\sim 80\text{--}100^\circ\text{C}$ until a dry thick brown sol was formed. This was further decomposed on hot plate at a temperature of 250°C to obtain dry black material. The polymeric precursor was calcined at 350°C for 4 h. The resulting powder was separated into parts and pressed in the form of pellets and sintered at 600 and 1000°C for 4 h. The samples sintered at 600 and 1000°C are referred to as L 600 and L 1000, respectively.

Results and Discussion:

XRD was performed on a Diffractometer (PANalytical XPERT-PRO) using Cu-K_α radiation at 40 kV and 30 mA . The data were obtained between 20 to $70^\circ 2\theta$, in steps of 0.02° and with scan step time of 1 second . XRD patterns for both the samples are shown in figure 1. The results indicate that both the samples sintered at 600 and 1000°C are single phase in nature. The X-ray diffraction data confirm the rhombohedral structure in a hexagonal lattice for both the samples. The corresponding lattice parameter ($a=b$) values are 5.498 \AA and 5.483 \AA for L 600 and L 1000 respectively. The lattice parameter ' c ' is found to decrease from 13.339 \AA (for L 600) to 13.3154 \AA (for L 1000). The calculated values of the unit cell volume are 349.18 \AA^3 (for L 600) and 346.70 \AA^3 (for L 1000). This result suggests that the shrinkage of the unit cell volume takes place with an increase in sintering temperature. This may be due to the shortening of Mn-O bond length at higher sintering temperature. It is clear from figure 1 that as the sintering temperature increases, there is a decrease in the full width at half maximum (FWHM) and hence the crystallite size increases. The average crystallite sizes of the samples are obtained by the X-ray line width using standard Scherrer's formula. The average crystallite size of a sample sintered at 600°C is calculated to be $\sim 19\text{ nm}$. The same increases to $\sim 28\text{ nm}$, for the sample sintered at 1000°C .

The grain size of the sol-gel prepared samples was determined by the atomic force microscopy (AFM) in contact method (as shown in figure 2). The images confirm the granular, dense structure with aggregate grains for both the samples. The average value of grain size is $\sim 64\text{ nm}$ (for L 600) and $\sim 118\text{ nm}$ (for L 1000). This indicates that the grain size increases with sintering temperature. The temperature dependence of resistivity at zero field in temperature range $25\text{--}300\text{ K}$ for the L 600 and L 1000 samples is shown in figure 3. The resistivity of the sample increases as the sintering temperature or grain size decreases. We observed that the sintering temperature strongly affects the T_{MI} even after the same chemical composition. The values of T_{MI} are $\sim 147\text{ K}$ and 246 K for the samples L 600 and L 1000 respectively. The magnetic field dependence of MR for both the samples were studied in magnetic field ranging from $0\text{--}8\text{ T}$ at 5 K and 300 K (as shown in figure 4). From figure 4, it is clear that the higher MR% is observed for sample L 600 (with smaller grain size). This enhancement in MR may arise due to intergrain spin-polarized tunneling across the grain boundaries [6].

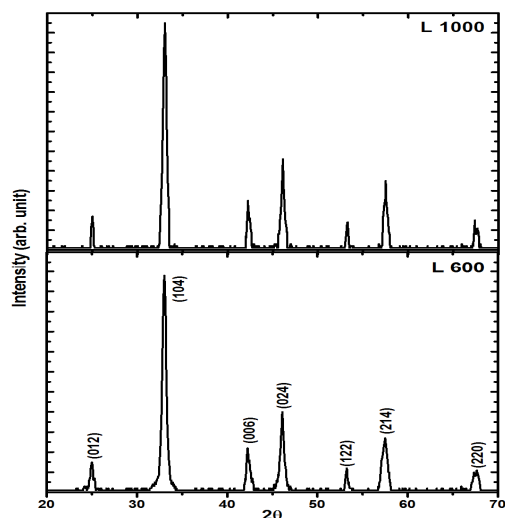


Figure.1: XRD Patterns of (a) L 600 and (b) L 1000.

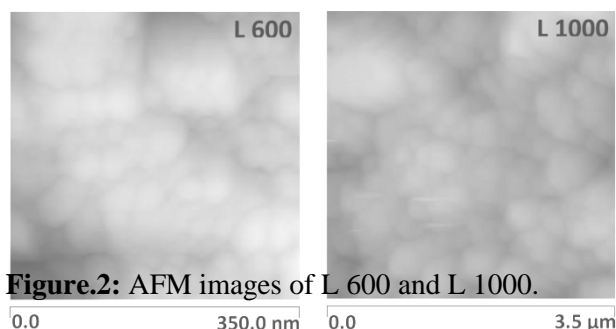


Figure.2: AFM images of L 600 and L 1000.

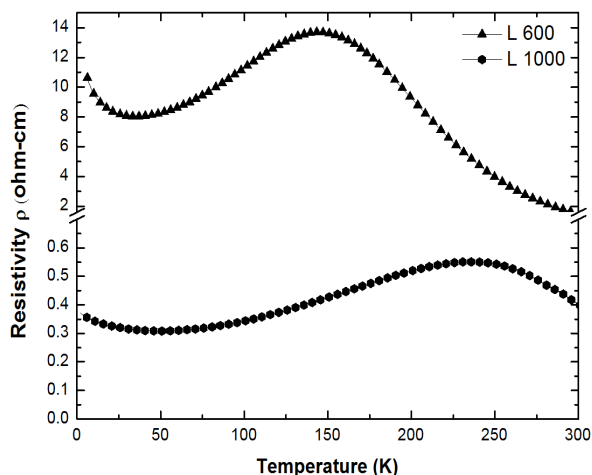


Figure.3: Plots of resistivity vs. temperature for L 600 and L 1000.

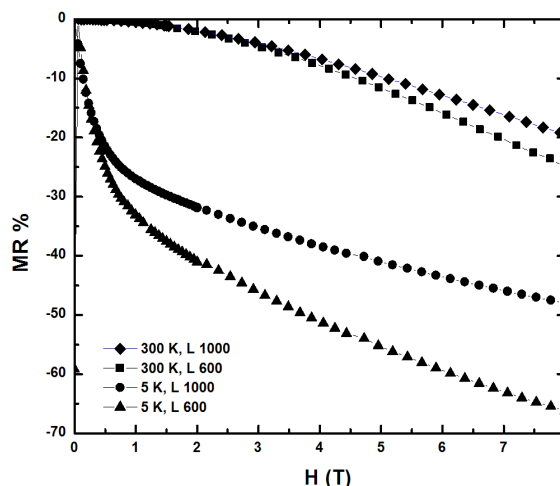


Figure.4: MR % vs. H(T) behavior of L 600 & L 1000 at 5 K and 300 K.

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