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EFFECT OF SINTERING TEMPERATURE ON STRUCTURAL AND CMR PROPERTIES OF $La_{0.8}Na_{0.2}MnO_3$

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ABSTRACT

Structure and grain size of $La_{0.8}Na_{0.2}MnO_3$ compound influenced by the sintering temperature is important to study because of correlation between the structural and magnetoresistive properties. In the present study, the crystalline structure of LNMO was studied at different sintering temperatures viz. 600 & 1000 °C and the samples were prepared by newly modified Lower Sintering Temperature Technique. These samples were characterized using X-ray diffraction (XRD) and crystallite sizes were calculated using Scherrer's formula and the values are in nano-scale. Isothermal Magnetoresistance (MR) measurements were carried out at 5 K, 50 K and 100 K between 0 to 5 T magnetic field. The influence of sintering temperature/crystallite size was observed on MR properties of LNMO samples sintered at various temperatures. The variation in MR behavior for both the samples is discussed in the framework of inter-grain spin-polarized tunneling across the grain boundaries.

Keywords: *LNMO nanoparticles, XRD, Magnetoresistance, Isotherm, Grain boundary and CMR*

INTRODUCTION

The discovery of the colossal magnetoresistance (CMR) effect in the perovskite manganites $La_{1X}A_XMnO_3$, where A is alkaline-earth-metal or alkali-metal element, have been extensively investigated due to its scientific interest and potential applications in various devices such as hard disk read heads and magnetic field sensors [1-3]. The previous work was focused mainly on the manganites, doped with divalent elements such as Ca, Sr, Ba and Pb, etc. at A site. In these types of compounds, variation of an element, keeping La concentration constant, leads to change in the Mn^{+3} content and in turn hole concentration and hence band filling is varied. There are only few reports on transport, magnetic and magnetoresistance properties of monovalent (like A = Na, K, Rb etc.) doped manganites. Due to the difference in valency, monovalent doping in $LaMnO_3$ can result in notably different outcomes. 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. [4, 5].

Therefore, the study of monovalent doping will offer au understanding on the structure and transport properties of doped $LaMnO_3$ manganites. 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 physical research as well as for potential applications [6, 7]. In the present case, Na^{+1} is selected as monovalent doping at La site in $LaMnO_3$ compound. $La_{0.8}Na_{0.2}MnO_3$ (LN) was sintered at two different temperatures 600 °C (LN6) and 1000 °C (LN10). The detailed study was carried out using XRD and isothermal measurements for better understanding of effect of hole doping by Na^{+1} in CMR compound sintered at various sintering temperature or prepared with different crystallite sizes.

EXPERIMENTAL

In the present work, we prepared the nanophasic $La_{0.8}Na_{0.2}MnO_3$ using Modified Lower Sintering Temperature Method. Polyacrylamide (PAM) was first dissolved in a beaker of deionized water and acetic acid which is referred as PAM solution. La acetate, Na acetate and Mn acetate (Sigma-Aldrich, purity ⩾ 99.9%) were added to the PAM solution with the concentration ratio of 0.8:0.2:1.0 to prepare a composition of $La_{0.8}Na_{0.2}MnO_3$, which is referred to the LN precursor solution. The precursor solution was stirred by glass rod for few minutes to keep it homogeneous. In the first dry-off step, precursor solution was dried at 80 °C for 2 h. In second dry-off step, the obtained gel was heated at 120 - 150 °C for 2 h. Now the obtained material was ground for more homogeneous mixture. This powder was calcined at 600 °C for 20 minutes in middle sintering step. The calcined powder was pelletized and sintered at 600^0 and 1000 °C temperatures for only 20 minutes and naturally cooled to room temperature inside the furnace.

RESULTS AND DISCUSSION

Sintering temperature is one of the key parameters that influences the crystallization of the perovskite LN samples, which in turn affects the magneto-transport properties. The crystallinity and phase analysis of both the synthesized samples were resolved by the powder X-ray diffraction, and the corresponding indexed patterns are shown in figure 1. X-ray diffraction (XRD) was performed on a diffractometer (PANalytical XPERT-PRO) using Cu-K_α radiation at 40 kV and 30 mA. The data was obtained between 20 to 80° 2θ, in steps of 0.02° and scan step time was 1 second. The analysis of XRD pattern shows that both the samples exhibit rhombohedral crystal system with the space group *R-3c*. The results indicate that all the samples sintered at various sintering temperatures viz. 600 and 1000 °C, correspond to pure LN single phase with no detectable secondary phases within the accuracy of measurements. The pure LN phase was obtained at a final sintering temperature as low as 600 °C. The values of the lattice parameters a, b, c and unit cell volumes V are listed in table 1.

We observed that the lattice parameters, unit cell volume, FWHM and maxima intensity were influenced with the variation in sintering temperature. The lattice parameters 'a' (a=b) and 'c' were found to decrease continuously, as the sintering temperature increases. Therefore, the volume of the unit cell also shrinks and unit cell becomes smaller with increasing sintering temperature. Similar phenomena were also observed by several groups in this type of CMR manganites [8, 9].

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We also observed a decrease in FWHM with the increase in sintering temperature. The decrease in the FWHM value, that is, increase in the sharpness of the XRD peaks, clearly indicates the improvement in the crystallinity with the sintering temperature [10]. The average crystallite sizes of the samples were determined from X-ray data using Scherrer's formula. Average particle size is calculated using equation $\tau = k\lambda/\beta\cos\theta$, where $k \sim 0.90$ is the shape factor, λ is the wavelength of X-rays, β is the FWHM and θ is the Bragg angle [11]. We observed the increment in average crystallite size as the sintering temperature increases. The calculated average crystallite sizes are listed in table 1. The XRD peak broadening due to the mechanical strain, instrumental error and other sources have been ignored in the calculation of the crystallite size.

The magnetic-field dependence of MR for LN samples was studied in magnetic-field range 0 - 5 T at 5 K, 50 K and 100 K as shown in figure 2. Analysis of figure 2 shows that with the increment in the magnetic field from 0 to 5 T, the MR of all the samples increases with negative values. The application of external magnetic field suppresses the magnetic spin scattering and also results into local ordering of magnetic spins. [12]. It is seen that MR falls suddenly with the increasing field in low-field region (~ 1 T). This is known as low field magnetoresistance (LFMR). This effect is more intense for sample LN10. The high values of LFMR were observed for both the samples. The spin polarized tunneling is responsible for this observation [13]. At comparatively high-field region (>1 T), MR value slowly increased linearly with the field, but with much reduced slope. The maximum high-field MR was observed at 5 K for LN10 sample. For LN6 sample, maximum MR was observed at 100 K. This high-field magneto-resistance (HFMR) can be regarded as resulting from non-collinear spins at grain boundaries. [14].

Moreover, as the sintering temperature decreases; the MR value increases at all constant temperatures. The maximum MR was observed for the sample LN6 (sintered at 600 °C). It was observed that the MR increased as the crystallite size/grain size decreased. It should be noted that the variation of MR does not show any saturation up to 5 T for both the samples. The maximum values of MR are 73% and 39% at 100 K and 5 K at a magnetic field of 5 T for LN6 and LN10 samples, respectively. This enhancement in MR for LN6 sample can be commonly interpreted within the framework of spin-polarized tunneling at the grain boundaries.

Table 1: The values of cell parameters, unit cell volume and crystallite size for LN samples.

Sample Code	Sintering Temp. (°C)	Lattice Parameters			Unit Cell Volume V (Å)^3	Average Crystallite Size (nm) (Scherrer's Formula)
		a (Å)	b (Å)	c (Å)		
LN 6	600	5.4997	5.4997	13.34	403.49	18
LN 10	1000	5.4821	5.4821	13.314	400.13	27

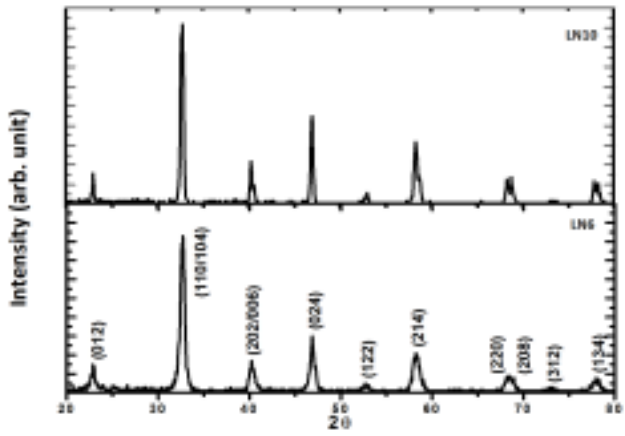

Fig. 1: Indexed XRD patterns for LN6 and LN10 samples.

CONCLUSIONS

We studied the effect of sintering temperature on the structural and isothermal magnetoresistance properties of nanophasic $La_{0.8}Na_{0.2}MnO_3$ manganites, which have been successfully synthesized by the lower sintering temperature technique. All the LN samples were single phasic having rhombohedral unit cells with R-3c space group. The unit cell volume decreases as we lower

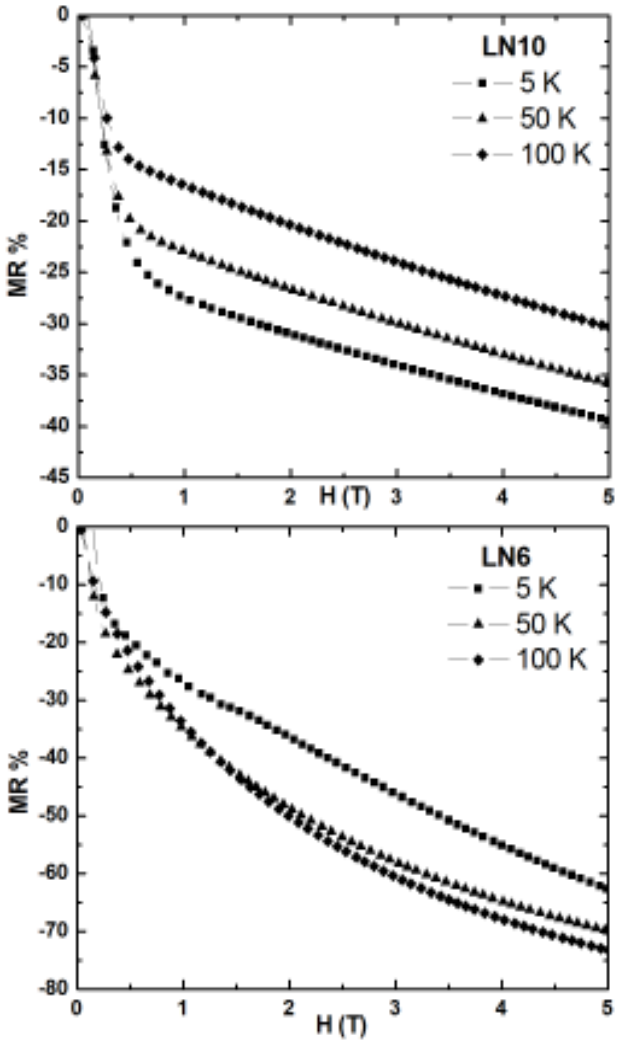

Fig. 2: MR vs. H(T) behavior of LN6 and LN10 at 5 K, 50 K and 100 K.

the sintering temperature. The high magnetoresistance was observed for the sample sintered at lower temperature with smaller crystallite size (LN6). The observed behavior was interpreted in terms of spin-polarized tunneling effect at grain boundaries.

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