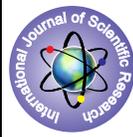


Impact of the sintering temperature on the structural and magnetoresistive properties of Nanophasic

$\text{La}_{0.70}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3$ manganite



Physics

KEYWORDS : magnetoresistance, sintering temperature, grain size, XRD

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ABSTRACT

A systematic investigation of the $\text{La}_{0.70}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3$ perovskite had been undertaken, mainly to understand the influence of the sintering temperature on the structural and magnetoresistance properties in this material.

The $\text{La}_{0.70}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3$ manganite was prepared by a modified auto-combustion method at 600 °C and 1000 °C. The X-ray diffraction studies show that both the samples are crystallized with the orthorhombic symmetry within the space group Pnma. The effect of sintering temperature was observed on lattice parameters, full width half maxima and crystallite size. The crystallite sizes and strain of the samples were determined using Hall-Williamson method. With increasing sintering temperature, the crystallite size increases, whereas the strain value decreases. Isotherm magnetoresistance (MR) measurements were carried out at various temperatures (5 K, 150 K, 200 K, 250 K and 300 K) between 0 to 8 T and strong impact of sintering temperature on MR was observed. The extrinsic MR effect might be responsible for such behavior.

INTRODUCTION

Over the last several decades, many materials exhibiting complex properties have been discovered. Out of many, manganites are very important materials for application point of view. In particular, manganites such as $\text{RE}_{1-x}\text{A}_x\text{MnO}_3$ (RE and A are trivalent rare earth and divalent alkaline earth elements respectively) attract a great interest of the scientific community because of the rich physics. They exhibit the various interesting properties like charge order/disorder, metal-insulator phase transitions, paramagnetism/ferromagnetism, structural distortion and particularly colossal magnetoresistance (CMR). The origin of such properties is the result of the close interplay of lattice, charge, and spin degrees of freedom.

A number of previous studies have looked at grain size dependence in the $\text{La}_{0.67}\text{A}_{0.33}\text{MnO}_3$ system. Hossain *et al.* [1] studied the influence of grain size on magnetoresistance of bulk $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (with larger grain size) manganite as a function of metal-insulator transition temperature, magnetic behavior and magnetoresistance. They have found the drastic changes in all these properties by varying the grain size. They kept the grain size in the range of a few micrometers and the variation in the values of transition temperature was very small (266.2 K for 3.3 μm and 266.8 K for 20.4 μm grain size). Venkataiah *et al.* [2] studied the effect of sintering on electrical transport properties of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ for smaller grain size (in the range of few nanometers). The shifting of T_{MI} was observed towards high temperature as the sintering temperature/grain size increased. In the case of smaller grain size (in the range of few nm), the variation of transition temperature was large (145 K for 20 nm and 195 K for 40 nm grain size). The variation of grain size was also ascribed to the observed effect on magnetoresistance value.

From these studies, it is clear that the value of magnetoresistance is sensitive for the sintering temperature/grain size. There are only few reports on transport, magnetic and magnetoresistance properties of monovalent (like A = Na, K, Rb etc.) doped manganites. Bhattacharya *et al.* [2] synthesized K doped $\text{La}_{1-x}\text{Ca}_x\text{K}_y\text{MnO}_3$ ($x=0.3$ and $0 \leq y \leq 0.15$) by the solid state reaction method. The electrical and magnetic transport properties of this system was investigated and it was observed that, this system having T_{MI} nearer to room temperature. In the present study, $\text{La}_{0.7}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3$ (CK) was selected as the chemical composition of the sample. We focused on the synthesis of a series of CK samples at different sintering temperatures (600 and 1000 °C) using the auto-combustion technique. The experimental probes like XRD and isotherm magnetoresistance were used for better understanding of the effect of sintering temperature/grain size for CMR compound doped by K⁺.

EXPERIMENTAL

The modified auto-combustion method was used for the preparation of CK samples. The $\text{C}_6\text{H}_5\text{LaO}_6 \cdot x\text{H}_2\text{O}$, $\text{Ca}(\text{C}_2\text{H}_3\text{O}_2)_2$, $\text{KC}_2\text{H}_3\text{O}_2$, $(\text{CH}_3\text{COO})_2\text{Mn} \cdot 4\text{H}_2\text{O}$, acetic acid, deionized water and ethylene glycol (EG) were used as raw materials to prepare $\text{La}_{0.7}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3$. First, according to molar ratio of composition, the solution of metal acetates was prepared with ethylene glycol, deionized water and acetic acid. The resulting mixture was continuously stirred and kept at 70-90 °C for a sufficient period of time to allow the La-Ca-K-Mn-EG gel formation. Then, the crucible reactor was placed on a hot plate to keep the temperature about 250 °C. At this stage, the gel was gasified and auto ignited with the descent of a large volume of gases to produce loose powder. After this, loose powder was calcined at 400 °C for 4 hours. The final sintering was performed at 600 °C (CK 600) and 1000 °C (CK 1000) to produce CK manganite samples with different crystallite size.

RESULTS AND DISCUSSION

PANalytical XPERT-PRO Diffractometer is equipped with $\text{Cu-K}\alpha$ X-ray radiation source (wavelength 1.54 Å) and detector with $\theta - 2\theta$ diffraction was used for the structural investigation. The data were obtained between 20 to 80°, in steps of 0.02° at room temperature. The x-ray patterns of two representative samples with the sintering temperature at 600 °C and 1000 °C of CK samples are shown in figure 1. It has been observed that all the samples of the present investigation crystallize in single-phase orthorhombic crystal structure with space group "Pnma". The obtained lattice parameters are listed in table 1.

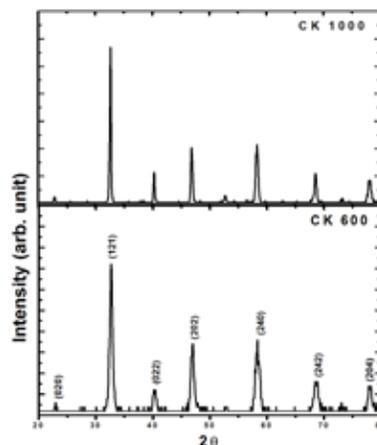


Figure 1: Indexed XRD patterns of CK 600 and CK 1000.

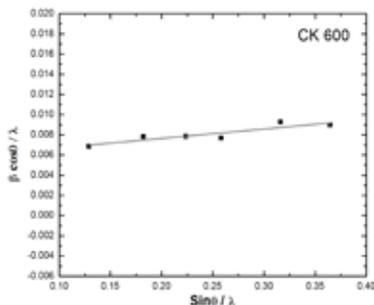


Figure 2: W-H Plot of $\beta \cos\theta/\lambda$ Vs. $\sin\theta/\lambda$ for CK 600.

We observed that the lattice parameters, FWHM and Bragg's angle (2θ value of maxima) are influenced by sintering temperature. The lattice parameter 'c' is found to continuously decrease, as the sintering temperature increases. 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 [4, 5]. We also observed a decrease in FWHM with the increase in sintering temperature. The decrease in the FWHM value, that is, an increase in the sharpness of the XRD peaks and variation in relative intensities, clearly indicates the improvement in the crystallinity with the sintering temperature [6]. The average particle sizes of the samples were also determined from X-ray data using Scherrer's formula [7]. The average particle size was calculated using equation $k\lambda/\beta \cos\theta$, 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's angle. We observed the increment in average particle size as the sintering temperature increases. The calculated average crystallite sizes are listed in table 1. We followed the Williamson-Hall approach to calculate particle size and lattice strain (ϵ). According to this method, the full width at half maxima (β) can be expressed as a linear combination from the strain (ϵ) and crystallite size (D) through the relation; $\beta \cos\theta/\lambda = k/D + \epsilon \sin\theta/\lambda$. Williamson-Hall plot of CK600 is shown in figure 2. As shown in the figure, a plot of $\beta \cos\theta/\lambda$ as a function of $\sin\theta/\lambda$ will give a straight line with a slope of strain ϵ and intercept on Y-axis will be equal to k/D . The crystallite size and strain values calculated from the graphs are listed in table 1. Line of Williamson-Hall plot has a slope, which indicates both the strain effect as well as size effect both is present. From the obtained values, it is clear that as the sintering temperature increases, the strain value decreases while crystallite size increases.

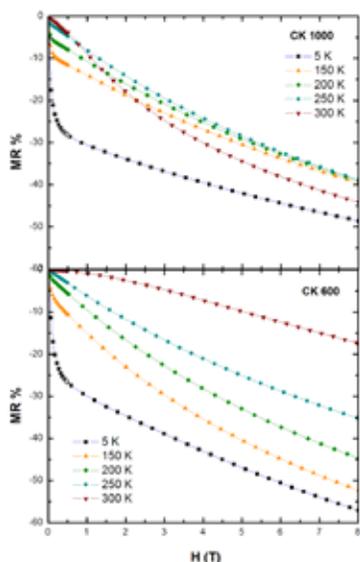


Figure 3: MR vs. H(T) behavior at 5 K, 150 K, 200 K, 250 K and 300 K for CK 600 and CK 1000.

In order to investigate the effect of sintering temperature on MR for CK samples, the isotherm measurements were carried at various temperatures (5 K, 150 K, 200 K, 250 K and 300 K) between 0 T to 8 T. The graphs of MR % vs. magnetic field at constant temperatures are shown in figure 3. As shown in the figure, the percentage of MR increases with increasing magnetic field. This can be explained by considering the effect of magnetic spins scattering in presence of application of magnetic field and resulting from the local ordering of the magnetic spins. [8]. All the samples show good low field magnetoresistance (LFMR) and the value is almost constant $\sim 30\%$ at 1 T for all the samples at 5 K. This indicates that the grain size effect on MR is less pronounced at such low temperature in this case. In high field region (>1 T), MR value slowly increases linearly with the field, but with a much reduced slope. The maximum high-field MR was observed at 5 K for all the CK samples. Sample CK 600 gives the highest MR value ($\sim 58\%$ at 8 T) for 5 K, whereas the values are less for the samples sintered at high temperature. This enhancement in MR for CK 600 sample can be commonly interpreted within the framework of spin-polarized tunneling at the grain boundaries.

TABLE - 1
VARIOUS PARAMETES FOR CK 600 AND CK 1000.

Parameters	CK 600	CK 1000
Final Sintering Temperature	600 °C	1000 °C
a (Å)	5.4381	5.4515
b (Å)	7.7409	7.7415
c (Å)	5.4945	5.4744
Crystallite Size (Scherrer's Formula) (nm)	~ 11	~ 13
Crystallite Size (W-H Method) (nm)	~ 16	~ 20
Strain (ϵ)	0.0093	0.0011

CONCLUSIONS

We could successfully synthesize phase pure $\text{La}_{0.70}\text{Ca}_{0.25}\text{K}_{0.05}\text{MnO}_3$ nanoparticles by a simple modified auto-combustion technique. The effects of sintering temperature on structure and magnetoresistance were investigated by XRD and isotherm magnetoresistance. Both the properties were strongly affected by sintering temperature/crystallite size. The various structural parameters were influenced by sintering temperature. The higher MR% was observed for the sample sintered at lower sintering temperature (or with smaller crystallite size). Due to the presence of smaller grains, more contribution of grain boundaries and therefore, the spin-polarized tunneling at grain boundaries may be responsible for this behavior. In addition, the present modified auto-combustion technique is a novel simple method to prepare manganite perovskites.

ACKNOWLEDGEMENTS

Authors are thankful to the departmental UGC DRS-SAP & DST-FIST programmes for providing some basic facilities. Some part of the samples' characterization was performed at UGC-DAE Consortium for Scientific Research, Indore. Help from Dr. R. Rawat of UGC-DAE CSR, Indore is thankfully acknowledged.

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