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On the Structural and Dielectric properties of sol-gel synthesized Copper doped Lanthanum Sodium Manganite (LNCMO) nanoparticles

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Abstract. $La_{0.7}Na_{0.3}Cu_xMn_{1-x}O$ nanoparticles (LNCMO for x=0, 0.05, 0.1) are prepared by a modified sol-gel auto combustion method. The structural analysis of samples fired at different temperatures are carried out using X-Ray Diffraction (XRD). From XRD patterns, it is observed that the structure of LNCMO nanopowders exhibited a perovskite rhombohedral structure for x=0 and 0.5 and orthorhombic for x=0.1. Temperature and frequency dependence of dielectric permittivity and ac conductivity of LNCMO samples are also investigated. The impact of copper substitution on the dielectric properties of LNCMO is elucidated. The increase in dielectric constant for LNCMO, for x=0 and x=0.05 with temperature and the decrease in LNCMO sample for x=0.1 are investigated as an effect of increase in copper doping. The variation in dielectric constant and ac conductivity with frequency and temperature of sample with x=0.1 indicated a phase transition associated with the sample near room temperature.

INTRODUCTION

Lanthanam manganite Perovskite materials doped with divalent alkaline earth elements have been used in many technological applications including magnetic recording, high density data storage, hard disks, magnetic sensors, spin electronic devices and magnetic refrigerants[1,2]. Perovskites are materials with chemical formula ABO_3 with A and B sites occupied by trivalent rare earth ions and divalent alkaline earth ions respectively. In the present study sodium is selected as dopant with respect to Calcium or Strontium, comes from the observation that the ionic radius of sodium is closer to the one of lanthanum. Even though it is possible to dope A site and Mn site in manganites, much research has been done on the substitution at A site with transition elements which can modify the Mn^{3+}-O-Mn^{4+} network and in turn will affect the intrinsic physical properties[3,4]. Copper has been selected as the dopant from the transition metals at the Mn site because of its variable valence. Review of literature shows that there are no reports on the properties of Copper doped Lanthanam Sodium Manganite (LNCMO) nanoparticles. In this work we have investigated the structural and dielectric properties of LNCMO nanoparticles

EXPERIMENTAL

Among the various methods used to synthesize the nanosized $La_{0.7}Na_{0.3}Cu_xMn_{1-x}O_3$ (LNCMO) particles, a modified sol-gel combustion method is adopted in the present work[5]. The precursors used for the synthesis of $LaNaCuMnO_3$ are Lanthanum nitrate ($La(NO_3)_3{*}6H_2O$), Manganese nitrate Mn $(NO_3)_2$, Cupper nitrate $Cu(NO_3)$, Sodium nitrate($Na(NO_3){*}H_2O$). In this process, the precursor solution is prepared by mixing metal nitrates in stoichiometric ratio, chelating agent (citric acid) and distilled water. The molar ratio of metal nitrates to fuel were 1:1. Solution is stirred well using magnetic stirrer at a temperature of 60^0C. After 20 minutes, Ethylene glycol in molar ratio 3:1 with citric acid is added to it. Then the solution is stirred continuously at 90°C until it became a gel due to the evaporation of water. The gel like substance is transferred to hot plate and the gel is burnt to obtain a black fluffy powder. The LNCMO samples are prepared for the concentrations of x= 0, 0.5 and 0.1. The powder samples obtained are grinded and calcinated at 1000^oC for 22 hours. The samples are made in the form of pellets

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using pelletizer for study of its dielectric constant at different temperatures. The pellets were finally sintered at 800°C for 3 hours.

CHARACTERIZATION

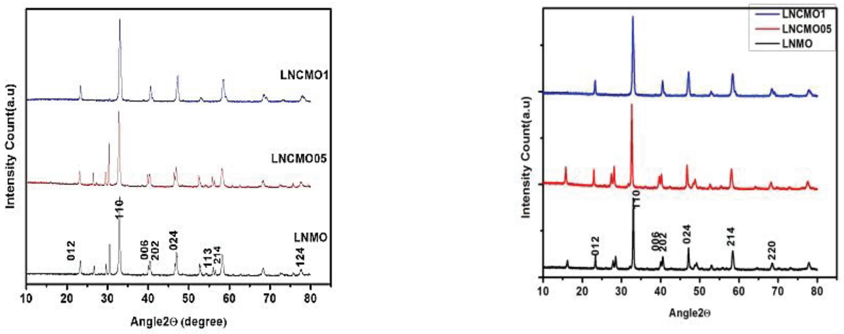
The structural characterization of the prepared powder samples are carried out by using PANalytical Aeris X-Ray powder diffractometer with Nickel filtered Cu-Kα radiation (λ=1.5418 A^0). The average crystallite size of samples is estimated by employing Debye Scherrer's formula[6]. The dielectric characterization of the samples are carried out by a Hewlett Packard 4192A LCR meter which is automated and controlled by a virtual instrumentation package called LabVIEW. The sintered pellets of samples with dimension of 2 mm thickness and 10mm diameter are used for the dielectric characterization. The capacitance, dielectric constant and ac conductivity are measured for frequencies ranging from 100 KHz to 5 MHz and in a temperature range of 303K to 333K. The sample temperature is controlled by a temperature controller and the temperature of the sample is sensed by an Iron-Constantan (Fe-K) thermocouple on the sample.

RESULTS AND DISCUSSION

Lanthanum Sodium Copper Manganite ($La_{0.7}$ $Na_{0.3}Cu_xMn_{1-x}O_3$) for copper substitution of x=0, x=0.05 and 0.1 nanopowders namely LNMO, LNCMO05 and LNCMO1 respectively were found to be greyish black in color and physically nonmagnetic.

Structural Characterization of LNCMO samples using XRD Analysis

The XRD patterns obtained for the samples after calcination for 12 hours and for 22 hours are shown in Fig 1(a) and (b) respectively. The perovskite structure of the samples were evident from the XRD patterns as reported in a number of Lanthanum Manganites.[7,8]. The crystal planes in the XRD patterns are identified to be that of typical Lanthanum manganite perovskites.



(a) (b)

FIGURE 1. XRD of samples calcined for (a) 12 hrs and (b) 22 hrs

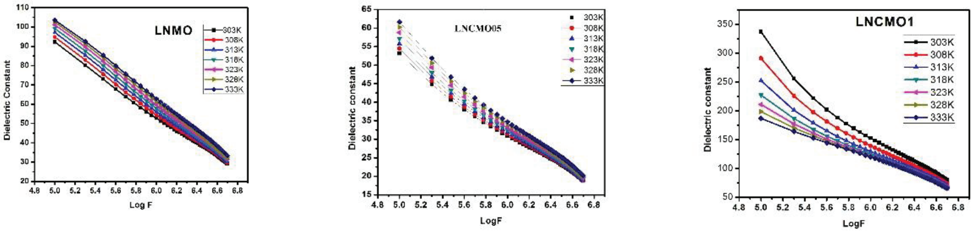
The LNMO and LNCMO05 samples found to possess a rhombohedral structure with double peaking behavior while LNCMO1 is found to be evidently orthorhombic in structure The significant crystal planes corresponding to the perovskite phase are{(012), (110), (006), (202), (220), (024), (214) and (124)}identified and indexed for both rhombohedral and orthorhombic phases of the samples. Some additional peaks which corresponds to impurity phase of oxides of Lanthanum are present in the XRD pattern of the samples LNMO and LNCMO05, but no additional peak is observed for LNCMO1. When the calcination time is increased to 22 hours, LNMO and LNCMO05 showed better peaks with reduced number of additional peaks. The LNCMO1 sample retained the same structure with improved crystallinity.

TABLE 1. Crystalline size of the samples from XRD pattern.

SAMPLE	Crystallite size (nm)	
	12 Hrs	22Hrs
LNCMO0	30.131	32.5412
LNCMO05	27.093	31.4866
LNCMO1	18.5923	20.2331

Dielectric Characterization of LNMO and LNCMO Samples

The dielectric properties of the samples like dielectric constant, and ac conductivity are measured as a tool to probe the prospects of the sample in electrical applications. The variation of dielectric constant with frequency and temperature for the three LNCMO samples are shown below. The dielectric constant decreases with increase in frequency and remains a constant at higher frequencies. Each dielectric mechanism has a characteristic relaxation frequency associated with the contributing dipoles of the frequency regime. A monotonic decrease in dielectric constant is known as dielectric dispersion is typical of interfacial polarization[9]. So in our frequency regime of measurements (100 kHz -5 MHz), it is the polarization due to interface dipoles which contribute to the overall dielectric properties of the sample. At higher frequencies, the frequency of electron/hole exchange will not be able to follow the applied electric field thus resulting in a decrease in polarization. Consequently the dielectric permittivity decreases. Plots for the variation of dielectric constant with frequency and temperature of the three samples is given Fig.2.

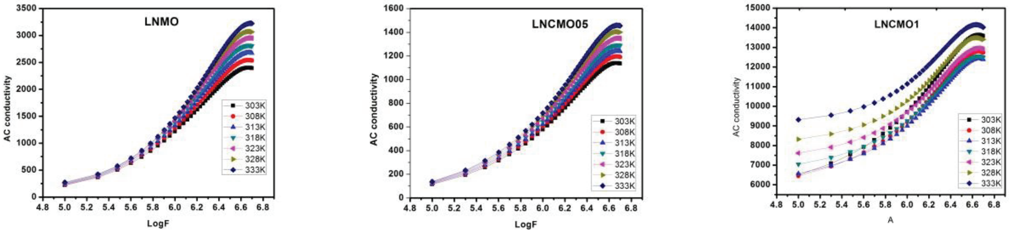


(a) (b) (c)

FIGURE 2. Variation of dielectric constant with Frequency for various Temperatures for (a) LNMO (b) LNCMO05 and (c) LNCMO1

The dielectric constant increases with temperature for the two samples LNMO and LNCMO05. As temperature increases the orientations of interface dipoles are facilitated and this enhances the dielectric permittivity. But for the sample LNCMO1 the dielectric constant has a maximum value at room temperature and decreases with temperature This type of behavior is observed in Manganites after a transition temperature[10]. It was observed that dielectric constant increased with the increase of Cu concentration and the dielectric constant is maximum at X=1.0 and minimum at X= 0. It is due to the fact that resistivity decreases with the increase in Cu concentration which increases the probability of electrons reaching the grain boundary. This increases the polarization and the probability of electrons reaching the grain boundary. This increases the polarization and hence the dielectric constant increases. For initial composition of x=0.05, this may not be significant due to the small percentage of substitution.

The ac conductivities of all samples increased initially and reached a broad maximum at higher frequencies as shown in Fig 3. The conductivity in manganite is essentially explained as due to the electron hopping between Mn^{2+} and Mn^{3+} and the hole hopping between Mn^{4+} and Mn^{3+}. As the frequency of the applied field increases, hopping of charge carriers also increases thereby increasing the conductivity. The presence of Mn^{4+} and Mn^{3+} in the perovskite structure results from the substitution of Na^{+} ions in the presence of La^{3+} ions. The presence of these multivalent Mn ions results in the observed variation in ac conductivity. Among the three samples conductivity is maximum for LNCMO1 sample. It is observed that for the two samples LNCMO0 and LNCMO05 the ac conductivity increases with temperature (Fig 3).The influence of temperature on AC conductivity may be explained by considering the mobility of charge carriers responsible for hopping whereas temperature increases, the mobility of hopping carriers increases that causes thereby an increase in conductivity .But for the sample LNCMO1 ac conductivity initially decreases reaches minimum value at 313K and then increases rapidly. The decrease in conductivity followed by an increase points towards the possible metal to insulator phase transition of the sample around the temperature.



(a) (b) (c)

FIGURE 3. Variation of ac conductivity with frequency at different temperatures for (a) LNMO, (b)LNCMO05 and (c) LNCMO1

CONCLUSION

Nanoparticles of $La_{0.7}$ $Na_{0.3}Cu_xMn_{1-x}O_3$ for x=0, 0.05, 0.1 (LNMO, LNCMO05, LNCMO1) prepared by a simple sol-gel auto combustion method. From the XRD patterns, it is observed that samples are perovskites with LNMO and LNCMO05 exhibiting rhombohedral structures with additional impurity peaks and LNCMO1 exhibiting an orthorhombic structure with absence of additional peaks. From the dielectric characterization as a function of frequency, the dielectric dispersion is observed to be typical of interfacial polarization. The observed temperature variation in dielectric constant of LNCMO1 point towards a phase transition associated with the sample below room temperature. A.C conductivity of the sample increases with increase of frequency. The variation of ac conductivity as a function of temperature is found to follow a different pattern for LNCMO1 sample which can be due to the different crystal structure phase associated with the sample compared with the other two samples. Hence variation in dielectric constant and ac conductivity indicated a phase transition associated with the LNCMO1 sample near 313 K. The observed characteristics recommend LNCMO1 sample for possible electrical applications of Manganites.

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