Journal of Science and Technology, Vol. 9 No. 3 (2017) p. 45-48

Effect of Cr-doped on Crystalline Phase, Surface Morphology and Electrical Properties of Charge-Ordered $Nd_{0.75}Na_{0.25}MnO_3$ Ceramics

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Received 30 September 2017; accepted 30 November 2017; available online 19 December 2017

Abstract: $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (x = 0, 0.02 and 0.05) ceramics have been synthesized using solid-state reaction method and the crystalline phase, surface morphology as well as electrical properties were reported. Powder X-ray diffraction analysis revealed all samples showed single phase and crystallized in an orthorhombic perovskite-structure whose unit cell belongs to the space group of *Pnma*. The increment of Cr content influenced the lattice parameters and the calculated unit cell volume; this is suggested due to the difference of ionic radius between Mn^{3+} and Cr^{3+} ions. Scanning electron microscopy image for sample with x = 0 shown the grains was in irregular shape and inhomogeneous causing the grain boundaries was not clearly seen compared to the x = 0.02 and 0.05 samples. The temperature dependence of the electrical resistivity measurement for all samples showed insulating behavior down to lower temperature under zero magnetic field for all samples. However, analysis of resistivity data of $d\ln\rho/dT^{-1}$ vs T shows a peak around 210 K and 160 K for x = 0 and 0.02 samples respectively. No such peak has been observed for x = 0.05 sample. This may be an indication the charge-ordered (CO) state was weakened by Cr-doped.

Keywords X-Ray Diffraction; Scanning Electron Microscope; Electrical Properties

1.0 Introduction

The hole-doped perovskite manganites with the general formula $Re_{1-x}A_xMnO_3$ where Re is trivalent rare-earth ion (La, Nd, or Dy), A is divalent alkaline earth ion (Ca, Sr, Cr or Ba) have received considerable attention due to the Colossal Magnetoresistance (CMR) effect which is commonly attributed with the double exchange (DE) mechanism [1]. Further studies demonstrated that, a monovalent-doped perovskite manganites showed the substitution of rare-earth by alkaline earth element leads to a mixed Mn^{3+}/Mn^{4+} state and induces a transition from paramagnetic-insulator to ferromagnetic-metallic phase [2,3]. Previous research on monovalent-doped manganites showed the astonishing manganite properties were closely related to a strong interplay between the magnetic, lattice, charge and orbital degrees of freedom [4]. In particular, the $Nd_{0.75}Na_{0.25}MnO_3$ compound has attracted due to the existance of charge ordering (CO) transition at relatively high temperature, T_{CO} ~ 170 K compared to antiferromagnetic (AFM) interaction [5].

Many reports showed that subsitution small amount of transition-metal element at Mn-site have a very effective ways to alter the properties of materials due to the changes of Mn^{3+}/ Mn^{4+} ratio [6]. For instance, the $Nd_{0.5}Ca_{0.5}Mn_{1-x}Cr_xO_3$ manganites reported that the CO and ferromagnetic transition were changed due to the effect of Cr doped in the compound. In addition, both electrical resistivity and magnetic susceptibility measurement showed that the CO insulating and FM metallic phases coexist in the compound [7]. Meanwhile, substitution of Cr at Mn-site in $La_{0.8}Ca_{0.2}Mn_{1-x}Cr_xO_3$ compound was reported to induce a metal-insulator (MI) transition temperature suggestively due to the weakening of DE mechanism [8]. Thus, considering all of the above, Cr doped for $Nd_{0.75}Na_{0.25}MnO_3$ is expected to change the resistivity data as well as weakened the CO state. However, such study on $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ compound is still limited.

In this paper, the effect of Cr doping on structure and electrical transport properties as well as as surface morphology of charge-ordered $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ceramics are

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reported. Result from density and porosity are also presented and discussed.

2.0 Experimental Method

The ceramics samples of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (x = 0, 0.02, and 0.05) were synthesized using conventional solid state reaction method. A stoichiometric amount of high purity (≥ 99.99%) Nd_2O_3, Na_2CO_3, MnO_2 and Cr_2O_3 were mixed and ground thoroughly by agate mortar and then calcined in air at 1000 °C using Protherm furnace Model PLF130/15 for 24 hours with several intermediate grindings process for 1 hour. The obtained powder were compacted into pellets with 13 mm diameter and 3mm thickness under a pressure of 4-5 tons and then sintered at 1200 °C for 24 hours. X-ray diffraction (XRD) was performed using Bruker D8 Advance model with a CuKα (1.544 Å) radiation at room temperature in order to confirm their structure. The sample was scanned continuously in the range of 20° ≤ 2θ ≤ 80° with a scanning rate of 2°/min. The XRD patterns were then analyzed by using X'Pert HighScore software to confirm the crystalline phase of the samples. Resistivity of the samples was using four-point probe method with silver point contact. The measurement was performed in a Janis model CCS 350T cryostat with temperature range of 20 – 300 K under zero magnetic field. The morphology of the synthesized samples was determined by using Phenom ProX, scanning electron microscopy (SEM) with 5000X magnification. Bulk density was determined by employing Archimedes principle using acetone as the buoyant medium.

3.0 Result and Discussion

The powder X-ray diffraction (XRD) patterns of all the samples are shown in Fig. 1. XRD analysis revealed all sample consist single phase and crystallized in orthorhombic crystal structure with *Pnma* space group [9]. Lattice parameters, unit cell volume (V), density (D) and porosity for all samples are tabulated in Table 1. It can be seen that, the values of V were observed to be decreased with Cr content. This can be suggested due to the possibility that Cr^{3+} ions with smaller ionic radius substituted Mn^{3+} ions with larger ionic radius in the lattice structure [10] and it is also supported the decreasing of D values with Cr doped.

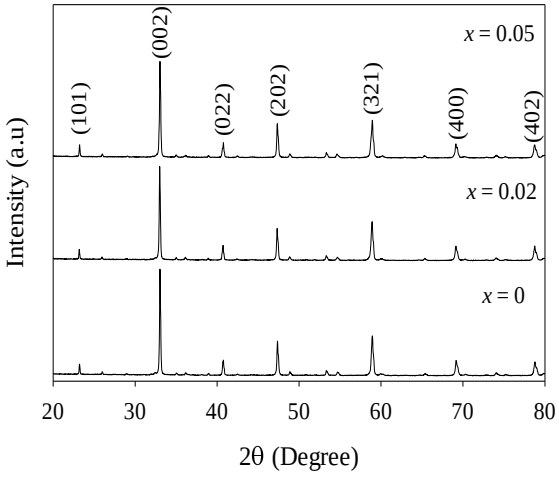

Fig. 1: X-ray powder diffraction pattern of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($0 \leq x \leq 0.05$) samples

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Table 1: Lattice parameters, unit cell volume (V), density (D) and percentage of porosity of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($0 \leq x \leq 0.05$)

Sample		x = 0	x = 0.02	x = 0.05
Lattice Parameter	a(Å)	5.446	5.437	5.448
	b(Å)	7.696	7.697	7.669
	c(Å)	5.445	5.450	5.443
V (Å)		228.2	228.1	227.4
D (g/cm^3)		5.97	5.96	5.88
Porosity (%)		5	6	7

Fig. 2 shows the effect of Cr-doped on temperature dependence of electrical resistivity for x = 0 – 0.05 samples. It was found that, all the samples showing the insulating behaviour in the temperature range of 140 – 300 K. Interestingly the analysis of resistivity data of $d\ln\rho/dT^{-1}$ vs T (inset Figure 2) showed a peak around 210 K and 160 K for x = 0 and 0.02 samples respectively while no peak was observed for x = 0.05 sample indicated the Cr-doped also affected the resistivity data in the region of CO state under zero magnetic field. Apart from that, the increasing of Cr content affected the intensity values of the resistivity which can be suggested due to the increase of carrier concentration as result of weakening the CO state [5].

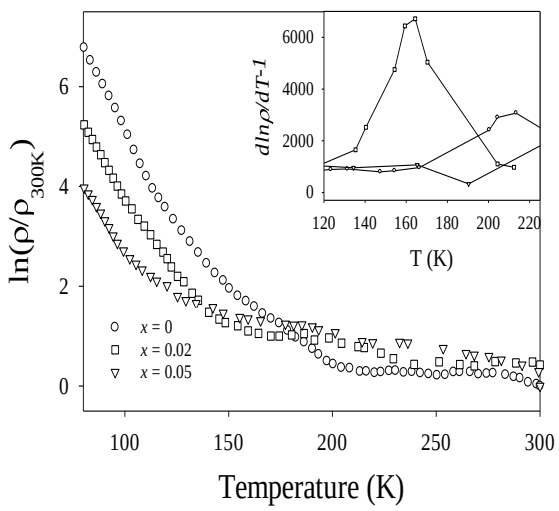

Fig. 2: Temperature dependence of electrical resistivity of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ ($0 \leq x \leq 0.05$). Inset is $d\ln\rho/dT^{-1}$ vs T for $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$

Fig. 3 shows the scanning electron microscope (SEM) micrograph of the $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (x = 0 – 0.05) samples with the magnification of 5000X. For x = 0 sample, illustrates that the grains were in irregular shape and inhomogeneous caused the grain boundaries not clearly seen compared to the x = 0.02 and 0.05 samples. Apart from that, further substitution for x = 0.02 sample, an increases in the average grain size was observed. It is can be suggested due to the difference of ionic radius between Cr^{3+} and Mn^{3+} affect the uniformity and disorder of the grain size of the [11]. However, the morphology study for x = 0.05 sample quite different compared to the x = 0.02 sample. This could be suggested probably due to the poor crystalline nature of these sample [12].

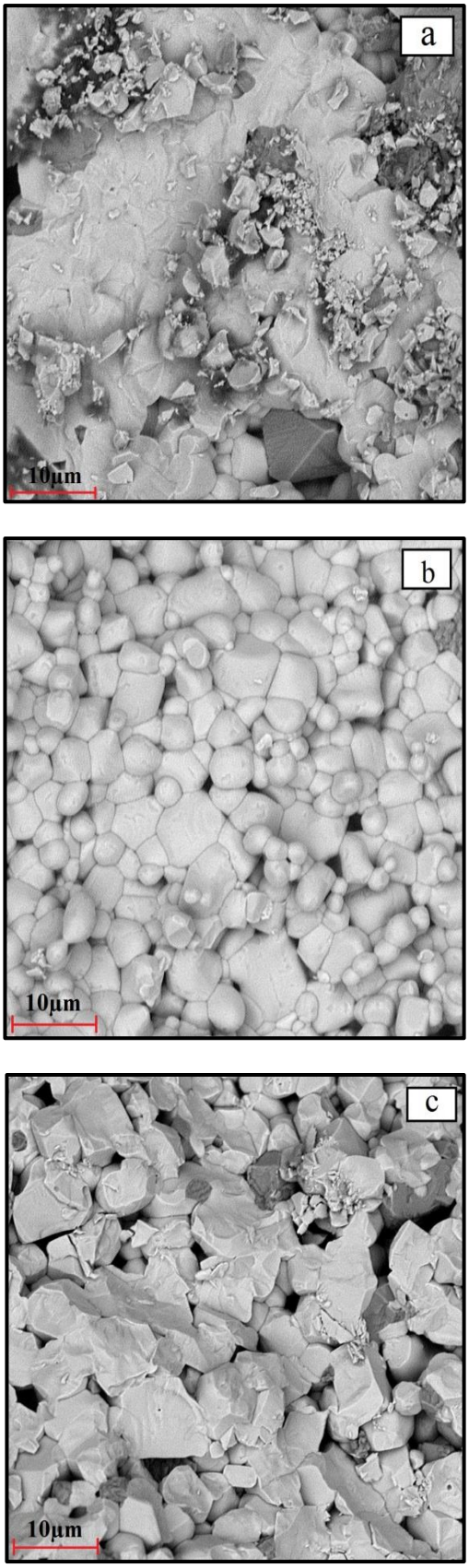

Fig. 3: SEM images with 5000× magnification for $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ samples (a) x = 0, (b) x = 0.02 and (c) x = 0.05

4.0 Conclusion

In conclusion, crystalline phase, electrical properties and surface morphology of the monovalent doped of $Nd_{0.75}Na_{0.25}Mn_{1-x}Cr_xO_3$ (x = 0, 0.02 and 0.05) samples have been investigated. Powder X-ray diffraction measurement shows all the synthesized samples were crystallized in the orthorhombic structure with *Pnma* space group. The dependence of the electrical resistivity measurement for all samples showing the insulating behavior. Analysis of resistivity data of $dln\rho/dT^{-1}$ vs T showed a peak around 210 K and 160 K for x = 0 and 0.02 samples respectively indicating the Cr-doped affected the resistivity data in the region of CO state. On the other hand, morphological study has shown the shape and grain sizes were affected by Cr doping.

Acknowledgements

This research was supported by RAGS/1/2015/STD/UTHM/03/1 grant Vot R060 from the Malaysian Ministry of Higher Education and was partly sponsored by the Centre for Graduate Studies UTHM.

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