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Crystalline Phase, Surface Morphology and Electrical Properties of Monovalent-doped $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ Manganites

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Abstract: Perovskite-type manganites $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ (y = 0 – 0.05) have been investigated to clarify the influence of Co-doped on crystal phase and morphological study as well as electrical transport properties. The $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ samples are prepared via solid state synthesis method. X-ray diffraction analysis revealed all the samples are essentially single phased and the peaks are indexed to an orthorhombic structure with *Pnma* space. The morphological study from scanning electron microscope shows the improvement of the grains boundaries and sizes as well as the compaction of particles can be seen as cobalt doping increased. On the other hand, the temperature dependence of electrical resistivity measurements using four-point-probe technique indicates all samples maintained an insulator like behaviour down to low temperature. Analysis of the resistivity change with respect to temperature, $d\ln\rho/dT^{-1}$ versus T reveals a slope changes of resistivity has been observed and a boarder peak exist for y = 0 sample and the peaks become significantly obvious for y = 0.02 and 0.05 samples. The peaks are observed in the range of charge ordering (CO) transition indicate the existence of CO in the system.

Keyword: X-ray diffraction; Electrical resistivity; Surface morphology.

1. Introduction

Extensive studies of manganese oxide perovskite with general formula $RE_{1-x}A_xMnO_3$ (where RE= Nd, La, Pr; and A= Ca, Sr) have been widely studied after the discovery of colossal magnetoresistance in these compound due to their unique properties as well as the potential application such as magnetic sensor at low temperature [1]–[3]. The mixed valency of Mn^{3+}/ Mn^{4+} of the perovskite oxide could be manipulated by changing the stoichiometric oxygen content or by partial substitution at either RE or A site [4], [5] which lead to the intriguing physical properties such as metal-insulator transition, charge ordering. $Nd_{0.75}Na_{0.25}MnO_3$ had been caught attention as it displays charge ordered at T_{CO} at area below 170 K [6].

The Mn site doping with other transition metal ions is believed to be an effective way to alter the properties due to the key role of Mn ions [5, 6]. For instance, P. Thamilmaran *et al*. reported substitution of Ni on $La_{0.7}Sr_{0.3}MnO_3$ reveals the transition of paramagnetic to ferromagnetic which leads to a decrease in Curie temperature, T_C as the concentration of Ni increased [9]. Metal-insulator transition, T_{MI} are observed in Ga-doped for $La_{0.7}Ca_{0.3}MnO_3$ and T_{MI} for each samples are shifted to lower temperature while resistivity increased as Ga increased due to the reduction of Jahn Teller Mn^{3+} in the parent compound [10].

Charge ordering which arises from the strong Coulomb interaction among electrons on the same Mn ion could be altered from small doping of cobalt (Co) in the manganese perovskite oxide [8]. Co is such a great candidate to be doped at Mn site due to the possibility of different oxidation states and multiple spin states [11]. In addition, the differences of ionic radius and electronic configuration between Co^{3+} (0.610 Å, $3d^6$), Mn^{3+} (0.640 Å, $3d^4$) and Mn^{4+} (0.53 Å, $3d^3$) make this study become more interesting as it will change the ratio of Mn^{3+} and Mn^{4+} as well as affecting the CO state [12].

B. Raveau *et al*. reported Co doping on $Pr_{0.5}Ca_{0.5}MnO_3$ system destroyed CO and induced metal-insulator transition in the

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compound [4]. The T_C of $La_{0.7}Ca_{0.3}Mn_{1-x}Co_xO_3$ has been reported to decreased from 260 K to 220 K probably due to the weakening of double-exchange mechanism [13]. Study of Co doping on of $La_{0.7}Sr_{0.3}MnO_3$ showed that T_C decrease with Co content which caused the reduction of ferromagnetic interaction and enhancement of antiferromagnetic interactions between Co and Mn ions [14]. Thus, considering all the information mentioned, a doping effect of Co at Mn-site of $Nd_{0.75}Na_{0.25}MnO_3$ is expected to alter the properties of the material as well as give a significant information about CO state. Such study of the Co doping on monovalent doped manganites, $Nd_{0.75}Na_{0.25}MnO_3$ has not been reported. This paper reports on the crystalline phase, microstructure and electrical transport properties in $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ ($0 \leq y \leq 0.05$) are reported with the aim to investigate the effect of Co doping on the CO state.

2. Experimental Method

Polycrystalline samples of $Nd_{0.75}Na_{0.25}MnO_3$ with doping level of y = 0, 0.02 and 0.05 are synthesized via solid state route. Stoichiometric ratio of Nd_2O_3, Na_2O_3, MnO_2 - and Co_2O_3 were mixed and ground thoroughly using agate mortar. The mixed powder was then calcined in air at 1000 °C for 24 hours using Protherm furnace Model PLF130/15 followed with intermediate grindings for an hour. The powder was pressed into pellets at 5 tons and sintered at 1200 °C for 24 hours in air.

The crystalline phase of all samples are investigated by Bruker D8, X-Ray Diffraction (XRD) at room temperature in the range of $20° \leq x \leq 80°$. The radiation utilized was Cu-Kα (λ = 0.15406 nm) which were operated at 40 KV and 40 mA. The XRD patterns were analysed using X'Pert HighScore software to confirm the crystalline phase of the samples. Scanning electron microscope (SEM), Phenom ProX with magnification 5kx were used to determine the surface morphology of the samples. Electrical resistivity for each samples were investigated by performing DC electrical resistivity measurement with four point probe technique utilizing Janis model CCS 350T cryostat and performed at temperature range of 20 – 300 K. Archimedes principle with acetone as an immersion liquid were conducted in order to determine the bulk density of the samples.

3. Results and Discussion

The XRD patterns of $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ perovskite samples with different compositions of y = 0, 0.02 and 0.05 are presented in Fig. 1. The diffracted XRD pattern analysis revealed that all samples were crystallized in orthorhombic crystal with space group of *Pnma* which are in agreement with the previous study [15]. Table 1 listed the value of lattice parameters, unit cell volume (V), density (D), and porosity of each samples. The nonexistence of the impurity peaks from the XRD pattern shows that all the visible peaks belong to a single crystalline phase. In addition, the lattice parameters and V seem to be decreased with Co content. This can be suggested due to successful replacement of smaller Co^{3+} ion into Mn site in the lattice structure [16]. Apart from that, the decreasing value for D and percentage of porosity with the increasing of Co content give a good agreement to the successful doping of Co ions in the system.

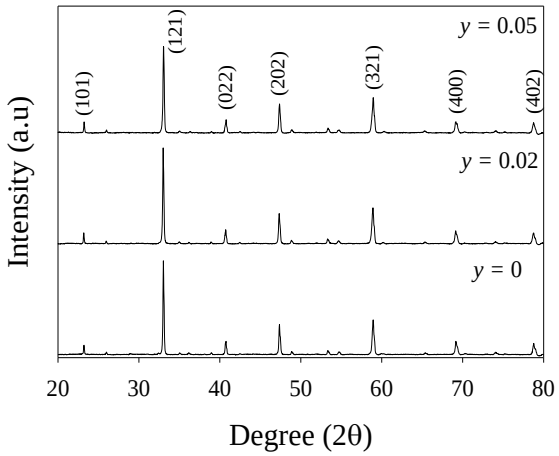


Fig. 1 XRD patterns for $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ ($0 \leq y \leq 0.05$).

Fig. 2 shows the temperature dependence of the electrical resistivity for the y = 0 – 0.05 samples. It could be seen that all the samples showing the insulating transport behavior in the region of 80 – 300 K and slight changes of the slope of resistivity data was observed below the temperature of 200 K. From the analysis of $dln\rho/dT^{-1}$ vs T curve (inset Fig. 2), a boarder peak around 215 K has been

observed for the $y = 0$ sample. Two clear peaks were found at temperature around 200 K and 235 K for $y = 0.02$ and $y = 0.05$ samples respectively. Interestingly, the location of the peaks was in the range of the charge ordering transition temperature and the transition shifted to higher temperature might be due to the existing of CO state [17].

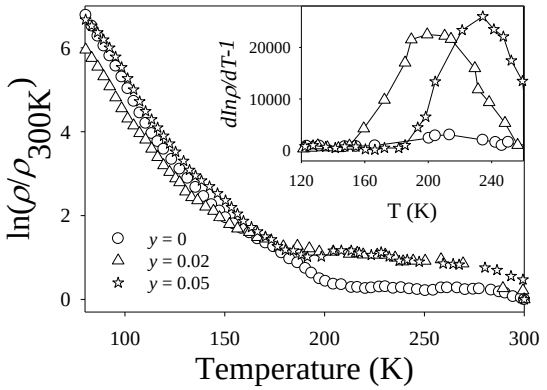
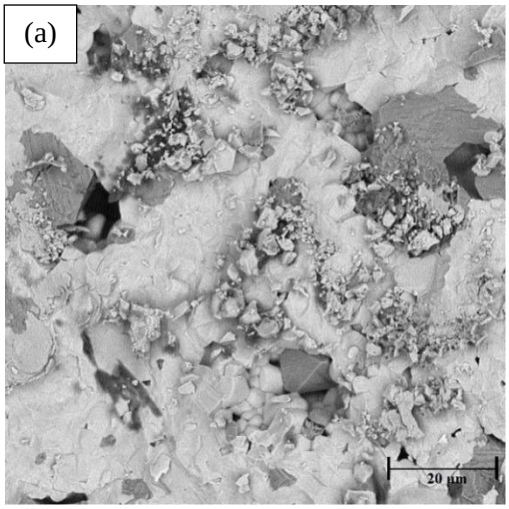


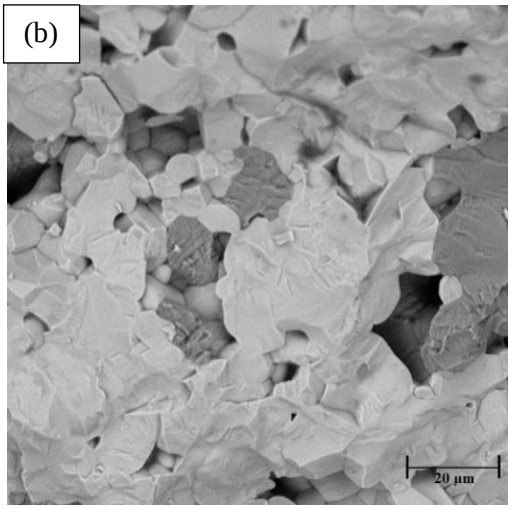
Fig. 2 Temperature dependence of electrical resistivity for $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ ($0 \leq y \leq 0.05$). Inset indicates the $d\ln\rho/dT^{-1}$ vs. T for $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$.

Table 1 Lattice parameter, unit cell volume, density and percentage of porosity for $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ ($0 \leq y \leq 0.05$) samples.

Sample		$y = 0$	$y = 0.02$	$y = 0.05$
Lattice Parameter	a (Å)	5.522	5.417	5.403
	b (Å)	7.670	7.649	7.640
	c (Å)	5.431	5.413	5.400
Unit cell volume, V (Å)		230.02	224.29	222.91
Density, D (g/cm^3)		5.9680	6.1263	6.1652
Porosity (%)		4.69	4.64	4.53

The microstructure of fractured samples were analyzed by SEM and the images for sample $y = 0$ - 0.05 are shown in Fig. 3 (a) - (c). For $y = 0$ sample, the grains are in irregular shape and there is no distinct grain boundaries observed. This can be suggested due to inhomogeneity of particles occurred during grinding process. In contrast, the grain size for sample $y = 0.02$ was started to be formed. Meanwhile, the improvement of grain boundaries can be observed by further doping for $y = 0.05$ sample and the grains seem to be well compacted compared to $y = 0$ and 0.02 sample. The improvement of the grain boundaries as well the compaction can be observed as the doping levels increased. This can be suggested due to the difference of ionic radii between Co^{3+} and Mn^{3+}. In fact, our finding is in agreement with previous study [12].





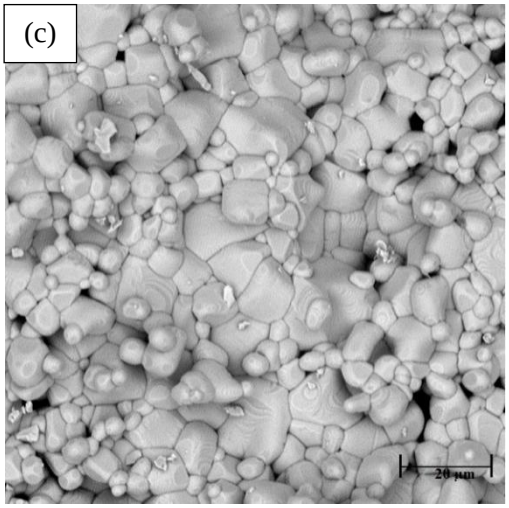


Fig. 3 SEM images with 5kx magnification for $Nd_{0.75}Na_{0.25}Mn_{1-y}Co_yO_3$ samples (a) $y = 0$, (b) $y = 0.02$ and (c) $y = 0.05$.

4. Conclusion

In conclusion, the effect of Co doping at Mn site of $Nd_{0.75}Na_{0.25}MnO_3$ ($y = 0$, 0.02 and 0.05) on structure, electrical and surface morphological have been investigated. From the study, the crystal structure of all samples were found orthorhombic with space group of *Pnma*. The decreasing value of lattice parameters, unit cell volume and density as Co increased can be suggested due to the replacement of Co ions into Mn site. Analysis of $d\ln\rho/dT^{-1}$ vs T from the resistivity measurement showed two distinct peaks at 200 K and 235 K for $y = 0.02$ and 0.05 samples respectively, indicating the existence of CO state in the sample. The SEM images indicate the inhomogeneity between the particles for sample $y = 0$. The grains and compaction of the particles improved as the Co^{3+} content increased which can be suggestively due to the difference of ionic.

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