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Research paper



Observation of Charge Ordering Signal in Monovalent Doped $Nd_{0.75}Na_{0.25-x}K_xMn_1O_3$ ($0 \leq x \leq 0.10$) Manganites

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Abstract

K doping in the compound of $Nd_{0.75}Na_{0.25-x}K_xMn_1O_3$ (x = 0, 0.05 and 0.10) manganites have been investigated to study its effect on crystalline phase and surface morphology as well as electrical transport and magnetic properties. The structure properties of the $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ manganite have been characterized using X-ray diffraction measurement and it proved that the crystalline phase of samples were essentially single phased and indexed as orthorhombic structure with space group of Pnma. The morphological study from scanning electron microscope showed there was an improvement on the grains boundaries and sizes as well as the compactness with K doping suggestively due to the difference of ionic radius. On the other hand, DC electrical resistivity measurement showed all samples exhibit insulating behavior. However, analysis of $d\ln\rho/dT^{-1}$ vs. T revealed the clearly peaks could be observed at temperature 210K for x = 0 and the peaks were shifted to the lower temperature around 190 K and 165 K for x = 0.05 and x = 0.1 respectively, indicate the existence of charge ordering (CO) state in the compound. Meanwhile, the investigation on magnetic behavior showed all samples exhibit transition from paramagnetic phase to anti-ferromagnetic phase with decreasing temperature and the T_N was observed to shift to lower temperature suggestively due to weakening of CO state

Keywords: *AC Susceptibility; DC Electrical; Scanning Electron Microscope; X-Ray Diffraction.*

1. Introduction

Perovskite-type manganites with general formula $R_{1-x}A_xMnO_3$, where R is rare earth metal (La^{3+}, Pr^{3+}, Nd^{3+}) and A is monovalent alkali metal (Li^+, Na^+, K^+) or divalent alkali metal (Ca^{2+}, Sr^{2+}, Ba^{2+}) has been extensively studied worldwide toward the understanding of the extraordinary structural, magnetic, electrical and thermal transport properties as well as the potential application at low temperature magnetic sensor material due to their high chemical stability, doping dependence of their magnetic transition temperature and colossal magneto-resistance (CMR) [1-6]. CMR effect is related to manganese-based perovskite oxides where the drastic change of their electrical resistivity behaviour in presence of magnetic field and can be interrelated to antiferromagnetic (AFM) super-exchange [7,8] , Jahn-Teller (JT) effect [9] and charge ordering (CO) state [10,11]. In particular, the $Nd_{0.75}Na_{0.25}MnO_3$ compound has received fair notable attention as it exhibits a CO transition at relatively high temperature, T_{CO}~170 K compared to AFM interaction [12,13]

For instance, K substitution in $Pr_{0.75}Na_{0.25-x}K_xMnO_3$ revealed a transition of metal-insulator (MI) as well as ferromagnetic to paramagnetic with increasing temperature from 50 K to 300 K suggestively due to the reduction in CO domain as a result of random distribution at A-site cations [14]. In addition, Shaikh et al. reported that all samples of $La_{1-x}Ag_xMnO_3$ induced a MI transition temperature suggested due to the destruction of CO state [9]. However, a clear understand on CO state in the monovalent-doped manganites is still limited.

On the other hand, surface morphology studies have been suggested as a successful tool in providing valuable information such as grain size and grain boundaries as well as porosity including manganites, which can help to show the interaction between morphological and structure study. For example, Zawawi et al. showed $Nd_{0.75}Na_{0.25}Mn_{x-1}Cr_xO_3$ for x = 0 sample, illustrates that the grain boundary and sizes was not clearly seen compared to x = 0.02 and x = 0.05 samples suggested probably due to the poor crystalline nature of these sample [15]. In addition, study on $Nd_{0.75}Na_{0.25}Mn_{y-1}Co_yO_3$ revealed that substitution of Co^{3+} leads to increment of grain size and grain boundary as well as improvement of compaction of sample suggestively due to the different of ionic radius between Co^{3+} and Mn^{3+} [10]. However, to the best of our knowledge study on K doped of $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ is not been reported. Hence, magnetic and electrical resistivity properties measured at low temperature would be very interesting to study as this could be reveal the information of CO state in the sample as well as provide a better understanding on the properties when another element was substitute at A-site of the compound.

This study reports on the DC electrical resistivity and AC susceptibility measurement on $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ ($0 \leq x \leq 0.10$) manganite with the aim to investigate the effect of partial K-doped on electrical transport and magnetic properties as well as provide understanding of CO in the material. Results from X-ray diffraction (XRD) and scanning electron microscopy (SEM) measurement as well as values of density and porosity are also presented and discussed.

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Table 1: Lattice parameter, charge-ordering temperature (T_{CO}), Neel temperature (T_N), unit cell volume (V), density (D) and percentage of porosity of $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ ($0 \le x \le 0.10$)

Samples	T_{CO} (K) (± 0.1)	T_N (K) (± 0.1)	Lattice parameter (± 0.001)			V(Å) (± 0.1)	D(g/cm^3) (± 0.01)	Porosity (%) (± 0.10)
			a (Å)	b (Å)	c (Å)			
x = 0.0	210.0	123.0	5.522	7.670	5.431	230.0	6.75	4.69
x = 0.05	190.0	115.0	5.656	7.622	5.416	233.5	7.83	4.30
x = 0.10	165.0	107.0	5.624	7.635	5.440	233.6	7.88	3.98

2. Materials and Methods

The standard conventional solid state reaction method was used to synthesis $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ (x = 0, 0.05 and 0.10) manganite samples by mixing high purity (≥ 99.99%) powder of stoichiometric quantities Nd_2O_3, Na_2CO_3, K_2CO_3 and MnO_2 in ambient atmosphere. The powders were carefully ground and calcined in air at 1000 ^oC for 24 hours with several intermediate grindings. Under load of 5 tons, the mixture powders then compacted into a pellet form with 13mm diameter and 2–3mm thickness. Finally, the samples in pellet form were undergoes sintering process at 1200 ^oC for 24 hours in air with heating rate of 15 ^oC/min and then slowly cooled at room temperature at rate of 1 ^oC/min to ensure better crystallization. All the finishing samples were then undergoes powder XRD measurement with CuKα radiation (1.5440 Å) at scanning rate 2 ^{0}C/min by using XRD Bruker D8 Advance model in room temperature condition. The XRD patterns was then analyzed by using X'Pert HighScore software to confirm the crystalline phase of the samples. The morphological study for prepared samples was determined by using Phenom ProX, scanning electron microscopy (SEM) with 5kX magnification. Investigation on transport properties were performed under zero magnetic field with silver paste contact in a Janis Cryostat Model CCS-350ST which utilizing four-point-probe method at low temperature. AC susceptibility measurement were operated at temperature 300 K down to 50 K and Signal Recovery 7265 lock-in amplifier were used to examine the real components. Bulk density of the samples was determined by employing the Archimedes principle using acetone as the liquid buoyant.

3. Results and Discussion

3.1. Structural analysis

The structure analysis for all the $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ (x = 0-0.10) samples had shown in Fig. 1. XRD study revealed all samples consist of significantly single phase without existing in impurity peaks were indexed as an orthorhombic structure with *Pnma* space group consistent with result reported from previous study [7,16]. From Table 1, it can be seen that the lattice parameter for all sample has no systematically trend due to the K substitution. However, the values of calculated unit cell volume (V) were found to slightly increase with K substitution. The small increase in calculated unit cell volume (V) point out the possibility that K^+ ions with larger ionic radius (r_{K+} = 1.550 Å) substitutes Na^+ ions with smaller ionic radius (r_{Na+} = 1.240 Å). A similar suggestion was also proposed for $Pr_{0.75}Na_{0.25-x}K_xMnO_3$ and $Pr_{0.55}Na_{0.05}Sr_{0.4}MnO_3$ [17,18]. Apart from that, the increasing in values of density (D) as well as decreasing in porosity with K content shows a good agreement with the slight increase in calculated unit cell volume (V) indicating a successful substitution of K^+ ions in the system.

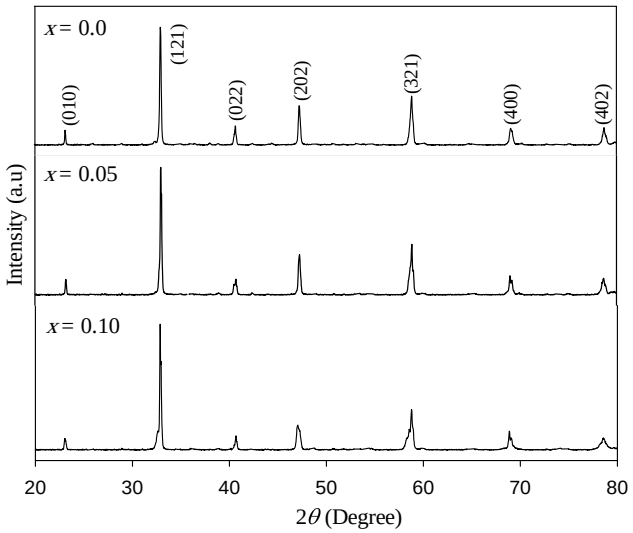
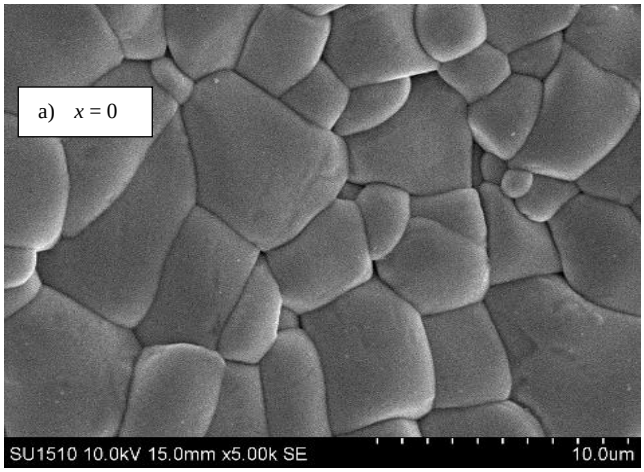
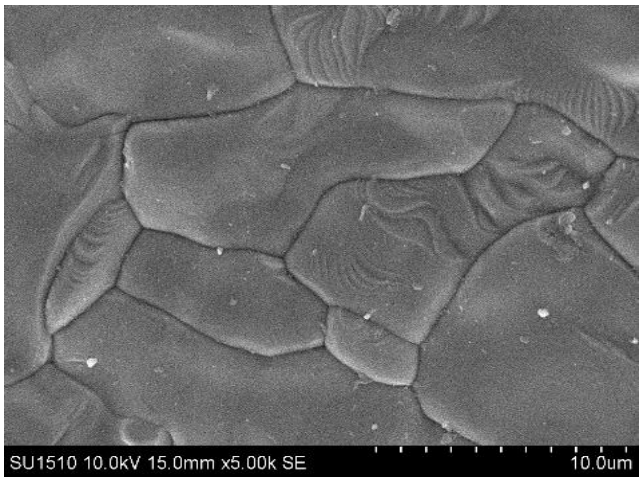


Fig 1: XRD pattern for $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ ($0 \le x \le 0.10$)

3.2. Morphology analysis

Fig 2. shows the results of scanning electron microscope (SEM) micrograph with 5kX magnification for all samples. It can be seen that, x = 0 sample showed an irregular shape compared to x = 0.05 and 0.10 samples. In addition, the grains seem like to be well compact for substitute samples suggestively successful substitution of K^+ ions in the compound as a result of difference in ionic radius between Na^+ and K^+ ions. In fact, our finding is in line with previous study [17]. Apart from that, the improvement of connectivity between grains was clearly seen as the doping levels of K increased.





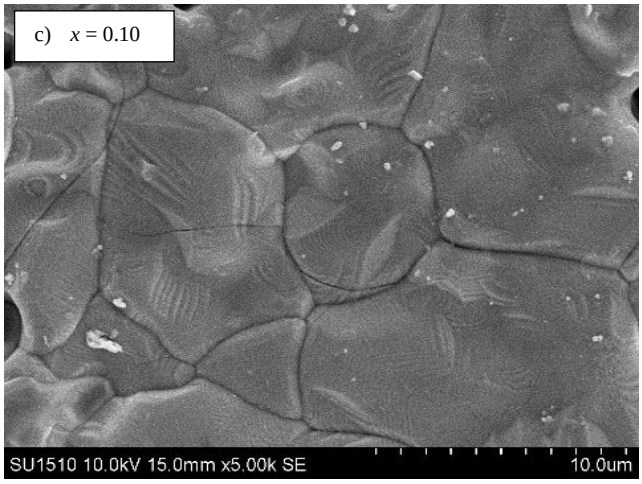


Fig 2: SEM micrographs (5kX) of $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ ($0 \le x \le 0.10$)

3.3. Electrical transport properties

Figure 3. shows the temperature dependence of electrical resistivity for the x = 0–0.10 samples under zero magnetic field. It was found that all samples showed insulating transport behaviour in the temperature range of 50–300 K. Interestingly, from the $d\ln\rho/dT^{-1}$ vs. T curve (inset Figure 3), a peak around 210 K and 190 K have been observed for x = 0 and 0.05 samples respectively while a broader peak was observed for the x = 0.10 sample around 165 K. Coincidently, the location of the peaks was in the range of the charge order transition temperature, T_{CO} as reported by Zawawi et al. and Fan et al. [15,19]. In addition, the shifting of the peaks from 210 K (x = 0) to 165 K (x = 0.10) samples indicate a weakening of CO state.

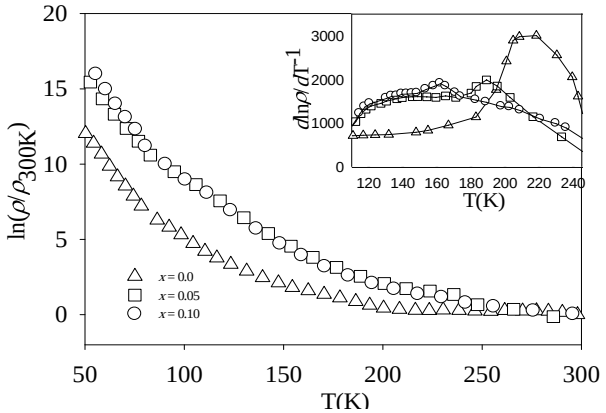


Fig 3: Temperature dependence of electrical resistivity for $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ ($0 \le x \le 0.10$). Inset indicates the $d\ln\rho/dT^{-1}$ vs. T for $Nd_{0.75}Na_{0.25-x}K_xMnO_3$

3.4. Magnetic properties

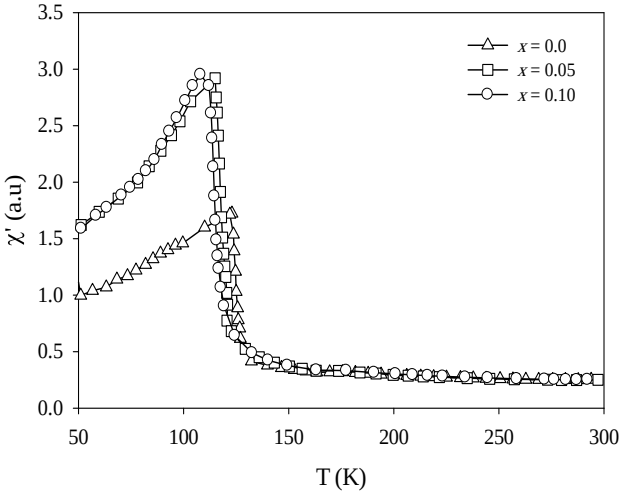


Fig 4: AC susceptibility versus temperature plot for $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ ($0 \le x \le 0.10$)

Temperature dependence of AC susceptibility (χ') measurements for all samples was shown in Fig 4. The AC susceptibility data revealed all samples exhibit paramagnetic (PM) to antiferromagnetic (AFM) transition with decreasing temperature. The Neel temperature, T_N was observed to decrease from 123 K, 115 K and 107 K for x = 0, 0.05 and 0.10 samples respectively suggestively due to a weakening of CO state in the compound. A similar suggestion was also proposed by Tarhouni et al. and Thaljaou et al. [20,21]. In the present study, the weakening of the CO state is also supported by the movement for peak of $d\ln\rho/dT^{-1}$ vs T curve for x = 0 and 0.05 samples.

4. Conclusion

In conclusion, the influence of K doped in $Nd_{0.75}Na_{0.25-x}K_xMnO_3$ ($0 \le x \le 0.10$) manganites has been studied. The values of calculated unit cell volume and densities increase continuously with K content and consistent with the SEM images which showed improvement on the grains boundaries and sizes as well as the compactness indicating a successful substitution of K^+ ions in the system due to the difference in ionic radius between Na^+ and K^+ ions. On the other hand, DC electrical resistivity and AC susceptibility measurements showed all sample exhibited an insulating behaviour and PM to AFM phase, where the transition temperature shifted to lower temperature from 123 K (x = 0) to 107 K (x = 0.10) in line with the observation of CO transition, T_{CO} in the compound suggestively due to weakening of CO state.

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